STUDIES IN THE CHEMISTRY OF BICYCLO[2.2.0]HEXANE

by

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B. S. in Chemistry, University of Kansas, 1964

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

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Manhattan, Kansas

1968

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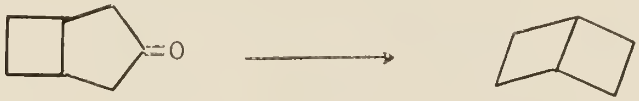
INTRODUCTION

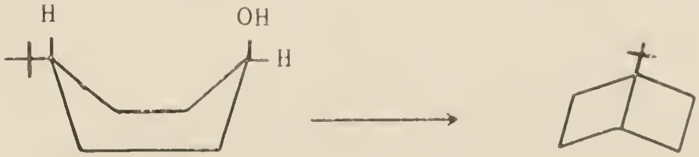
The interest in the formation and reactions of the bicyclo[2.2.0]hexyl system has sharply risen in the last two years. A review of the literature prior to early 1966 has been completed by C. E. Rieneke[72]. Now, as then, most of the published work deals only with the synthesis of the various compounds, and only recently have papers appeared which deal with reactions and solvolysis rates. Enough work has appeared though, to allow the compounds to be listed according to their basic ring structure.

Bicyclo[2.2.0]hexane (1), the simplest possible compound of this ring structure, was first prepared by Cremer and Srinivasan[23] by the photolytic elimination of carbon monoxide from bicyclo[3.2.0]heptan-2-one. Several other methods of preparation[43,95,99,104] have been used since then to prepare this compound. Most recently Baldwin and Gano[6] looked at the quantitative mercury-sensitized gas phase photolysis of norcamphor. They found that 1 was formed in only minor amounts; a result at variance with that previously reported[43].



1

The loss of water from *cis*- and *trans*-4-*tert*-butylcyclohexanol in the mass spectrometer was observed by Brion and Hall[12]. They found that the boat conformation of the *trans*-alcohol was required in the formation of 2.



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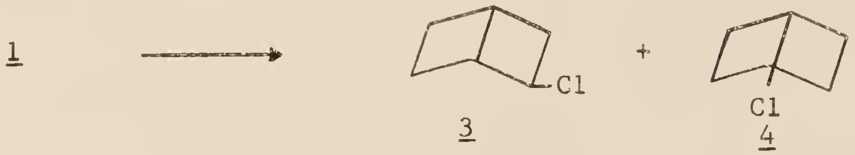
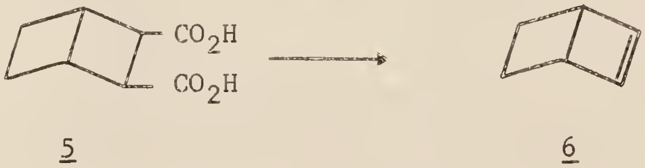
In 1967, Srinivasan and Sonntag[97] reported on the photochlorination of 1. Three of the four chlorinated products obtained were identified as 4-chlorocyclohexene, *exo*-2-chlorobicyclo[2.2.0]hexane (3), and 1-chlorobicyclo[2.2.0]hexane (4). The parent hydrocarbon 1 was produced by

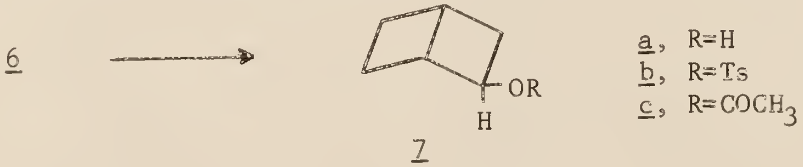


reduction of 3 with sodium and *n*-butyl alcohol.

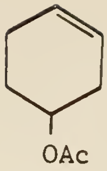
Bicyclo[2.2.0]hex-2-ene (6) was prepared by McDonald and Reineke[59] by oxidative bisdecarboxylation of bicyclo[2.2.0]hexane-2,3-dicarboxylic acid (5) with lead tetraacetate in pyridine.



McDonald and Reineke[59,61] reported the synthesis and solvolysis of *exo*-bicyclo[2.2.0]hex-2-yl tosylate (7b). The *exo*-alcohol 7a was prepared by hydroboration and subsequent oxidation of bicyclo[2.2.0]hex-2-ene (6).



The acetolysis rate constants for 7b were 1.92 ± 0.14 x 10^{-4} sec^{-1} at 90° and 4.24 ± 0.23 x 10^{-5} sec^{-1} at 75°. The acetolysis products were composed of 51% of 3-cyclohexenyl acetate (8), 41% of *exo*-bicyclo[2.1.1]hex-2-yl acetate (9), 5% of 2-cyclohexenyl acetate (10), and 3% of *exo*-bicyclo-



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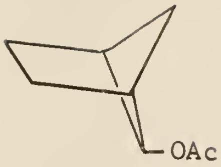

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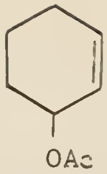

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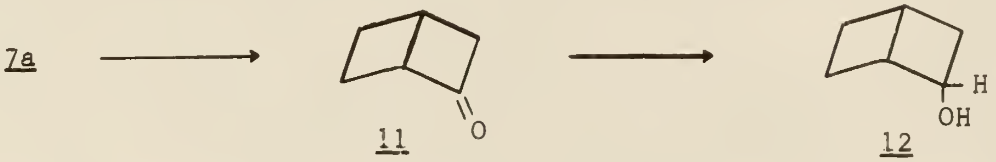
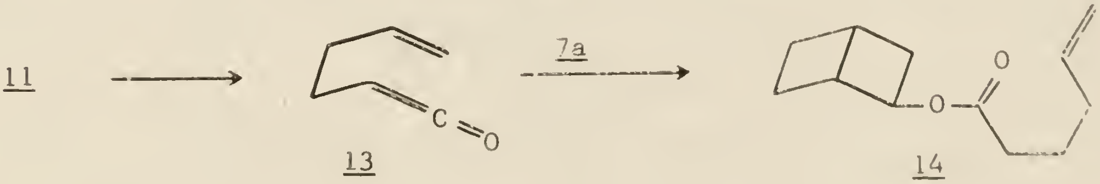
[2.2.0]hex-2-yl acetate (7c).

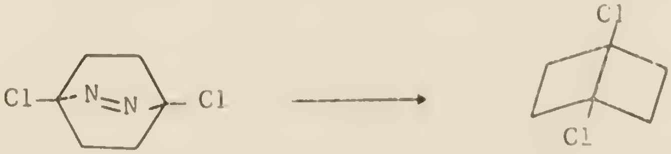
The synthesis of bicyclo[2.2.0]hexan-2-one (11) and *endo*-bicyclo-[2.2.0]hexan-2-ol (12) were later reported by McDonald and Reineke[60,62]. *tert*-Butyl hypochlorite oxidation of 7a at 0° gave 11, which could not be



isolated, but was observed spectrally and reduced to 12 with sodium borohydride. When the oxidation of 7a was performed at room temperature, 5-hexenoic acid and *exo*-bicyclo[2.2.0]hex-2-yl 5-hexenoate (14) were isolated. The formation of 14 was explained by the spontaneous ring-opening of 11 to 4-butenylketene (13) which would be trapped by 7a to give 14.



In 1966, Luettke and Schabacker[55] reported the synthesis of 1,4-dichlorobicyclo[2.2.0]hexane (15) by the photolysis of 1,4-dichloro-2,3-diazobicyclo[2.2.2]oct-2-ene in perfluoromethylcyclohexane.



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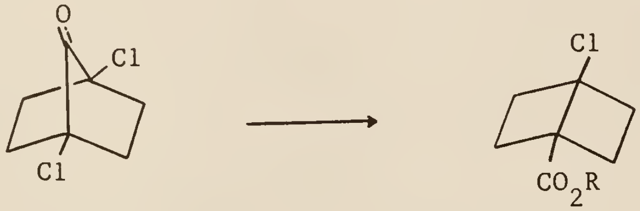
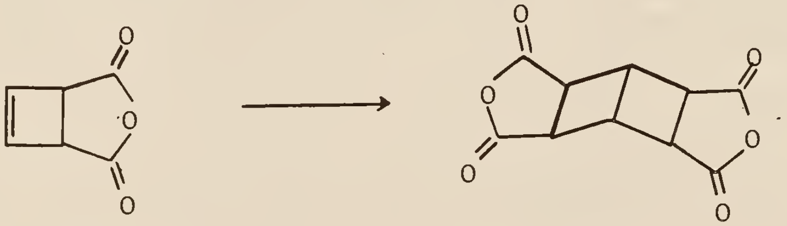
Scherer[86] reported the synthesis of 4-chlorobicyclo[2.2.0]hexane-1-carboxylic acid (17a) by the reaction of structure 16 with powdered sodium hydroxide in tetrahydrofuran. They found that gentle work-up conditions were essential if the acid was to be isolated in pure condition. It appeared that 17a was less stable than 17b which was much less stable than 1 itself. Some solvolytic reactions of 17a have also been described[87].



16 17

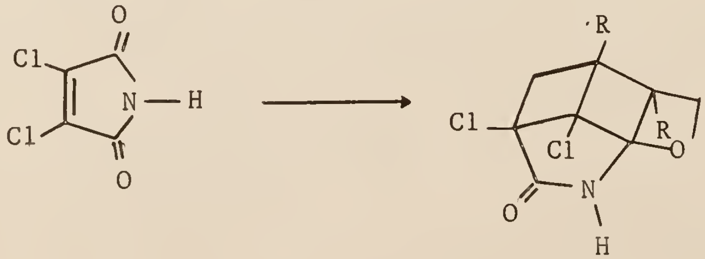
a, R=H
b, R=CH_3

Several tetrasubstituted bicyclohexanes have been recently prepared. Koltzenberg, Fuss, and Leitick[51] found that acetylene in the presence of benzophenone would react photolytically with maleic anhydride to produce 3-cyclobutene-cis-1,2-dicarboxylic anhydride (18). This compound would reach further with maleic anhydride to give 19.



18 19

Scharf and Korta[82] found that 2,3-dimethylbutadiene would react under photolytic conditions with dichloromaleimide to produce a highly substituted bicyclohexane of structure 20.



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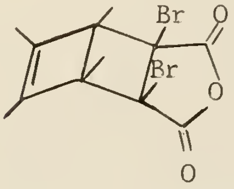
Another photochemical reaction was used by Criegee and Zanker[25] to prepare structure 22. 2,3-Diiodo-1,2,3,4-tetramethylcyclobutene and dibromomaleic anhydride were combined to give anhydride 21, which when allowed to react with sodium and methyl alcohol gave 22. Treatment of this compound with sodium bicarbonate followed by iodine and potassium iodide in water gave ester 23.



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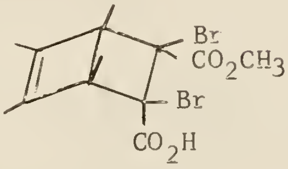

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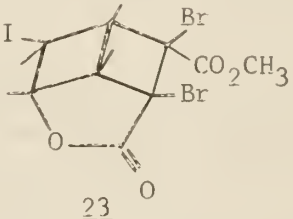
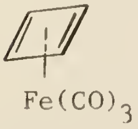


23

Oxidation of cyclobutadieneiron tricarbonyl (24) with ceric ion at 0° in the presence of dimethyl maleate produced dimethyl *endo*-bicyclo[2.2.0]-hex-5-ene-2,3-dicarboxylate (25)[108]. In the presence of dimethyl fumarate, diester 26 was produced. The structures of these esters were proven by ozonolysis followed by esterification to produce the corresponding 1,2,3,4-tetracarbomethoxycyclobutanes.



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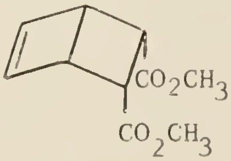

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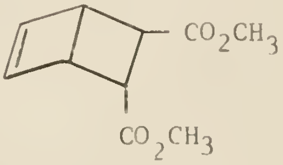

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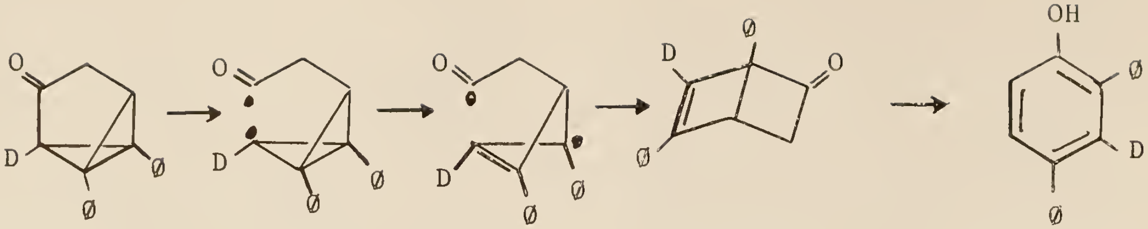
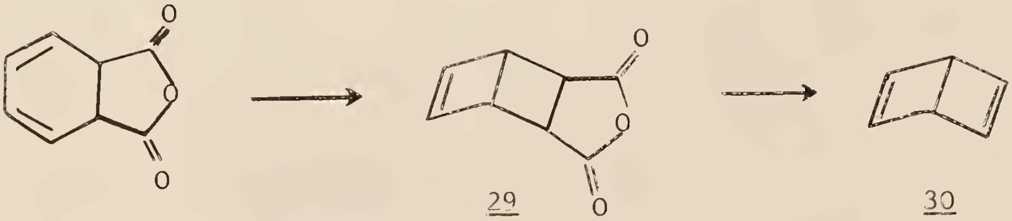
The photolysis reaction of structure 27 was reported in early 1966[57]. No scrambling of the deuterium was observed in the final product, 2,4-diphenylphenol, and for this reason the following mechanism was proposed using bicyclohexene 28 as a possible intermediate.



27

28

The first unsubstituted bicyclo[2.2.0]hexa-2,5-diene (30) was prepared by van Tamelen and Pappas[104] in 1963. The photolytic reaction of *cis*-1,2-dihydrophthalic anhydride produced the photoanhydride 29 which was decarboxylated to produce 30. The half life of 30 at room temperature was found to be approximately two days.



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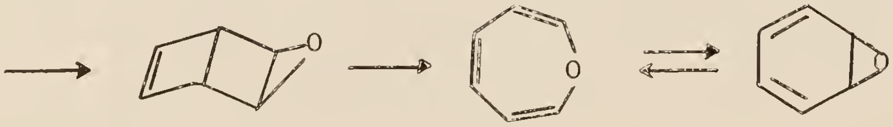
30

van Tamelen and Carty[105] studied some nonaromatization reactions of bicyclo[2.2.0]hexa-2,5-diene (30). They found that 30 would react with *m*-chloroperbenzoic acid to give epoxide 31, which after being heated at 115°, isomerized to oxepin-benzene oxide (32), and phenol, and would add one mole of bromine to give a mixture of dibromides 33 and 34 in a ratio of

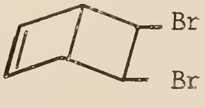
30



31

32

30:70, respectively.



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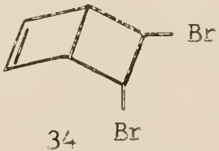
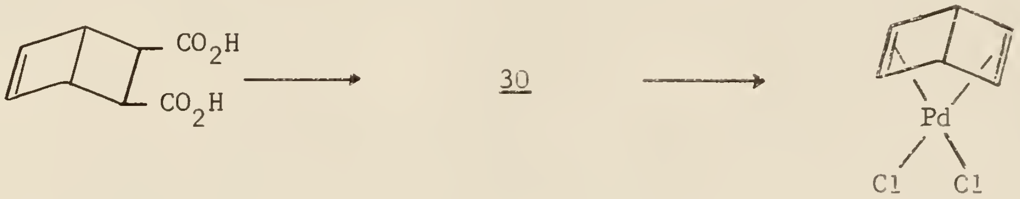


34

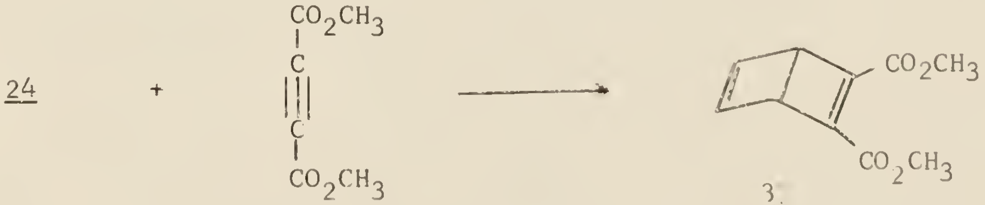
Recently van Tamelen and Carty[105] prepared the first metal coordination complex of a "Dewar benzene". The acid 35 was electrolytically decarboxylated to produce 30, which was reacted further with bis(benzonitrile)-palladium dichloride in methylene chloride to give structure 36.



35

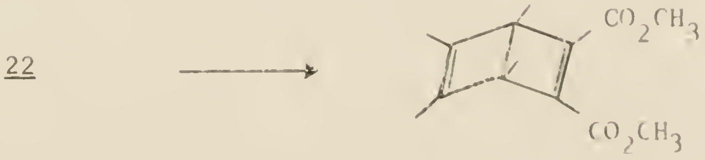
36

To date, the most versatile method of preparing functionally substituted "Dewar benzenes" is that devised by Watts, Fitzpatrick, and Pettit[107]. Their procedure involves the decomposition of cyclobutadieneiron tricarbonyl (24) with ceric ion in the presence of an acetylene. A number of substituted bicyclo[2.2.0]hexa-2,5-diene derivatives have been reported[14,107]. As an example where the acetylene is dimethyl acetylenedicarboxylate diester 37 is produced.



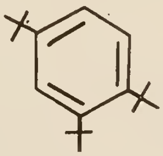
3

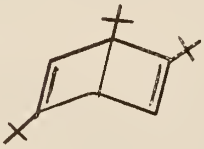
Criegee and Zanker[25] reported that dibromide 22, when esterified with diazomethane and allowed to react with zinc-copper couple in ether, would produce diester 38.



38

Wilzback and Kaplan[115] studied the photoisomerization of 1,2,4-tri-*tert*-butylbenzene using a light source of wavelength 2537 Å. The three major products were the "Dewar benzene" 39, the prismane 40, and 1,3,5-tri-*tert*-butylbenzene. They found that on continued irradiation, 39 produced 40, and 40 yields 39 and the two benzenes.





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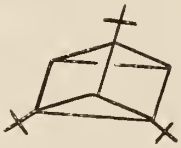

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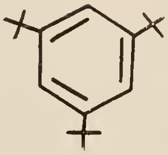
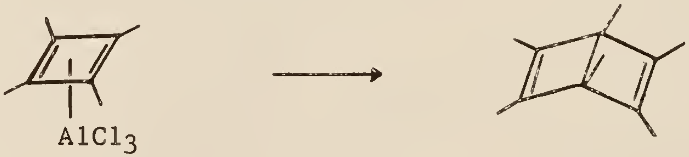
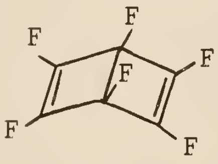


A one-stage synthesis of hexamethyl "Dewar benzene" (41) was reported by Schafer[81] in 1966. 2-Butyne was allowed to react with aluminum chloride in benzene to produce an intermediate cyclobutadienealuminum trichloride complex that reacted further to give 41.

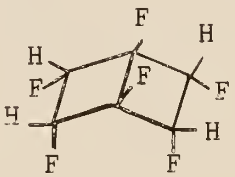


41

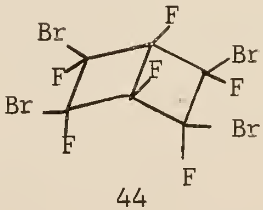
Both Haller[45] and Camaggi et al.[15] have observed the vapor phase photolysis of hexafluorobenzene and found that the product produced was perfluoro "Dewar benzene" (42).



42



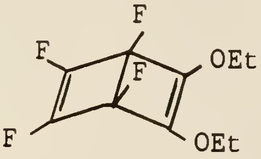
43



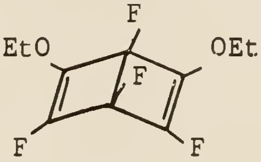
44

Camaggi, Gozzo, and Cavidalli[15] found that perfluoro 42 could be catalytically reduced to 43 with palladium on carbon. They also found that 42 would add two moles of bromine to give tetrabromide 44.

The ^{19}F magnetic resonance spectra of three diethoxytetrafluorobicyclo-[2.2.0]hexa-2,5-dienes (45, 46, 47) and the corresponding aromatic isomers were reported by Cavalli[17]. The chemical shifts and multiplet splittings of the signals were correlated with the molecular structure.



45



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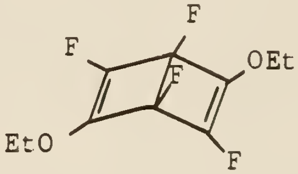
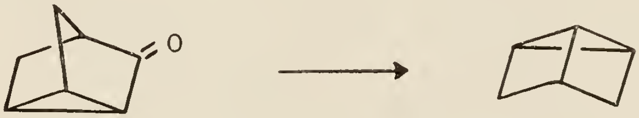


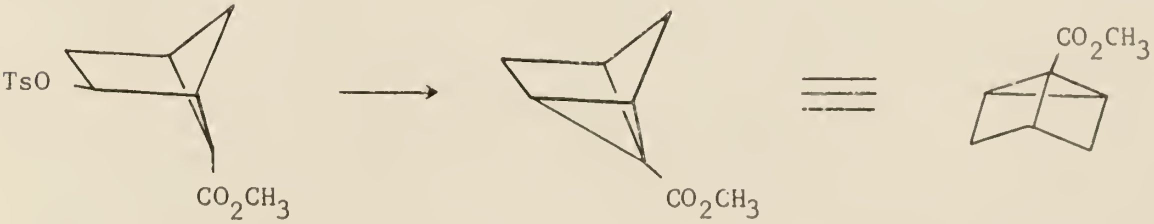
47

Tricyclo[2.2.0.0^{2,6}]hexane (48) was prepared in 1964 from the mercury-sensitized photolysis of nortricyclanone[53].



48

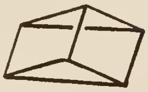
The only functionally substituted compounds of this tricyclic ring structure were reported by Meinwald and Crandall[63] in 1966. Methyl tricyclo[2.2.0.0^{2,6}]hexane-1-carboxylate (50) was prepared by base treatment of tosyloxy ester 49. Catalytic hydrogenation of the tricyclic acid corresponding to 50 gave rise to a single, liquid acid identified as cyclopentylacetic acid.



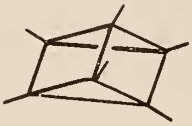
49

50

The only parent compound of a series not yet reported is tetracyclo-[2.2.0.0^{2,6}.0^{3,5}]hexane (51), although some substituted derivatives of it have been made. Both Lemal[54] and Schaefer[80] have looked at the photolysis reaction of hexamethyl "Dewar benzene" (41). Hexamethylprismane (52) and hexamethylbenzene were the only products observed. The prismane 52 on further irradiation gave 41 and the benzene derivative as products.

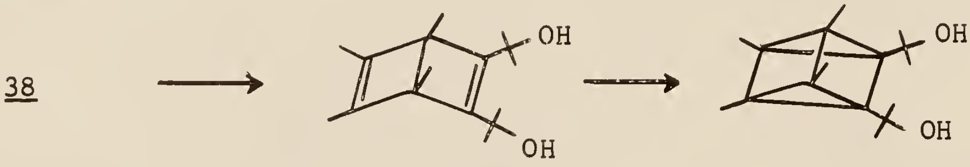


51



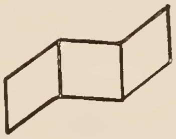
52

Early in 1966, Criegee and Askani[26] reported on the highly substituted prismane 54. Reaction of diester 38 with methylmagnesium iodide produced dialcohol 53. This compound produced structure 54 under photolysis conditions in ether.

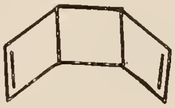


53 54

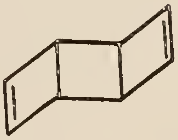
Several examples of larger ring systems incorporating the bicyclo[2.2.0]hexane frame-work have recently appeared. The simplest tricyclooctane was prepared by Srinivasan and Hill[96] by the irradiation of a solution of cyclobutene in acetone. The only hydrocarbon product was identified as anti-tricyclo$[4.2.0.0^{2,5}]$octane (55).



55



56

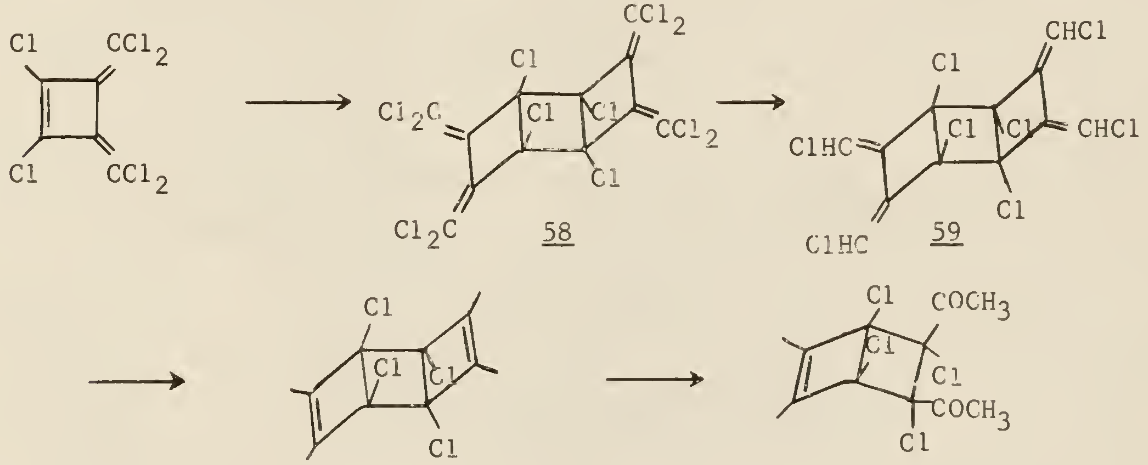


57

Watts, Fitzpatrick, and Pettit[108] observed the decomposition of cyclobutadieneiron tricarbonyl (24) in the absence of trapping agents and found a 5.1 mixture of syn- (56) and anti-tricyclo$[4.2.0.0^{2,5}]$octa-3,7-diene (57).

Mano et al.[56] found that pyrolysis at 160° of perchloro(3,4-dimethylenecyclobutene) affords perchloro-(3,4,7,8-tetramethylene)tricyclo$[4.2.0.0^{2,5}]$-

octane (58). This compound was reduced in acetic acid by heating with zinc powder to give structure 59 which was further reduced to the tetramethyl derivative 60 by hydrogenation over palladium-charcoal. Furuske et al.[41] found that the stereochemical configuration of 58 was exclusively of the anti form. Structure 60 was cleaved by ozone in methanol-carbon tetrachloride to diketone 61. However, the second double bond strongly resisted further ozonolysis.


Cl
CCl2
Cl
CCl2
CCl2
Cl
Cl2C
Cl
Cl
CCl2
Cl
Cl2C
CHCl
Cl
ClHC
Cl
Cl
CHCl
Cl
ClHC
Cl
Cl
Cl
Cl
Cl
COCH3
Cl
Cl
COCH3
Cl

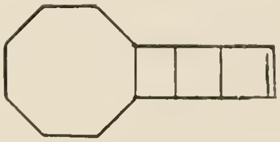
58

59

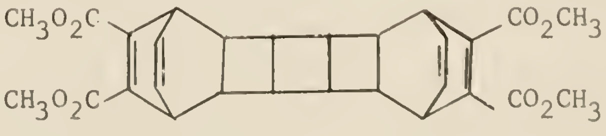
60

61

The photochemical 1,3-cycloaddition of cis-cyclooctene to benzene was reported in early 1966[13]. A minor component of the product mixture was identified as 62.



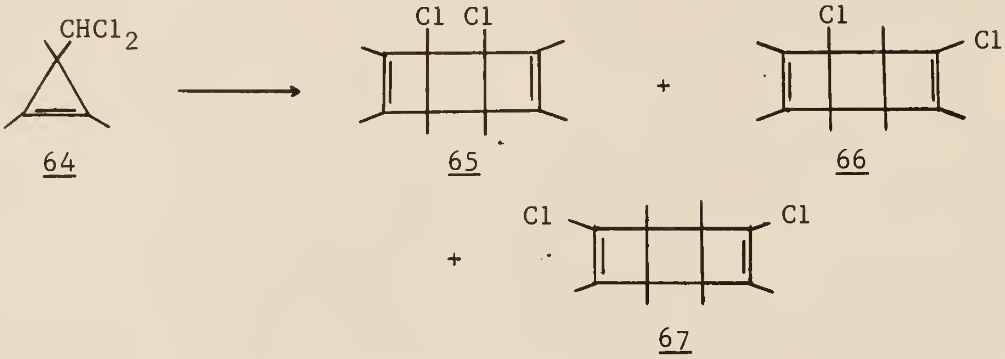
62


CH3O2C
CH3O2C
CO2CH3
CO2CH3

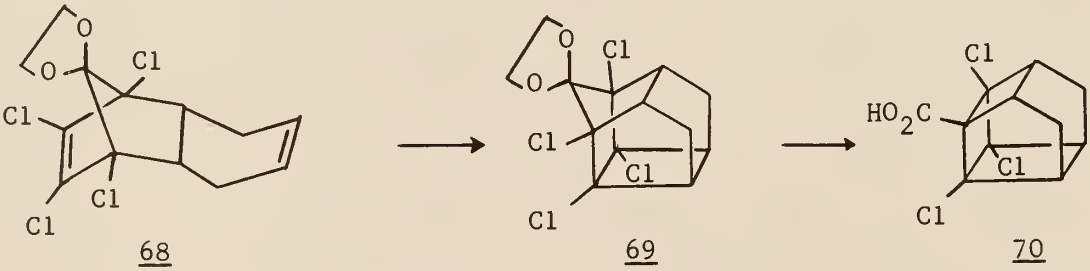
63

Schroeder and Martin[89], while investigating the structure of the cyclooctatetraene dimer of melting point 52°, found that it would accept two moles of dimethyl acetylenedicarboxylate to give tetraester 63.

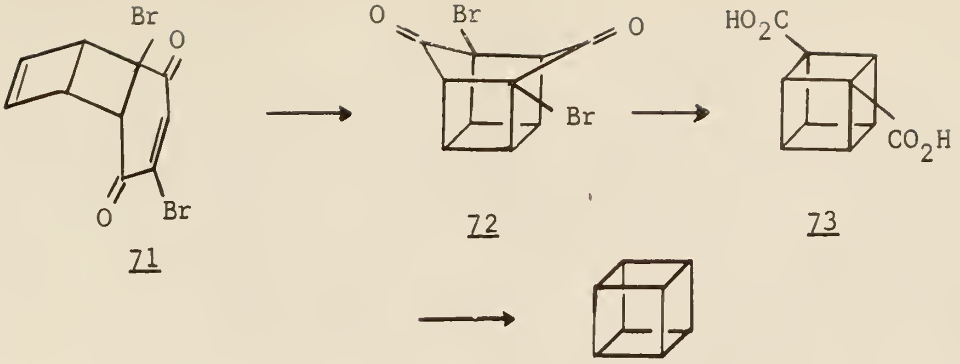
A mixture of four isomeric tricyclooctanes was obtained when cyclopropene 64 was allowed to react with n-butyllithium in ether at -20°[10]. A chlorocyclobutadiene was proposed as a reaction intermediate. Definite assignments of structure could not be made, but compounds 65, 66, and 67 are three of the possible products formed.



Stedman, Miller, and Hoover[98] reported that irradiation of diene 68 in acetone solution afforded an 82% yield of caged product 69. Treatment of this compound with sulfuric acid gave the corresponding ketone which was refluxed in toluene over solid sodium hydroxide to give a 65% yield of acid 70.

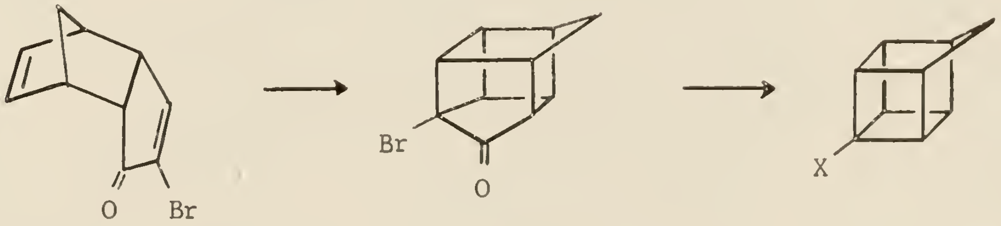


Cubane (74) was first reported in 1964 by Eaton and Cole[34]. Since that time only one other synthesis of this ring system has been published. Barborak, Watts, and Pettit[7] found that decomposition of cyclobutadieneiron tricarbonyl (24) in the presence of 2,5-dibromobenzoquinone yielded the Diels-Alder adduct 71. Irradiation of this compound in benzene afforded the colorless isomer 72 which was treated with aqueous potassium hydroxide at 100° to give cubane-1,3-dicarboxylic acid (73). Convincing proof of the structure of 73 was established through its decarboxylation to cubane (74) by thermal degradation of the di-tert-butyl perester.



71 72 73 74

Dunn, DiPasquo, and Hoover[33] reported the Diels-Alder reaction between cyclopentadiene and 2-bromocyclopentadienone to give adduct 75, which was cyclized photochemically. The intermediate pentacyclodecanone 76 was converted to homocubyl derivative 77a by a Favorskii ring contraction. The carboxyl group of 77a was eliminated by a modified Hunsdiecker reaction, and the product was dehalogenated to give the hydrocarbon, pentacyclo-$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$nonane (77b).

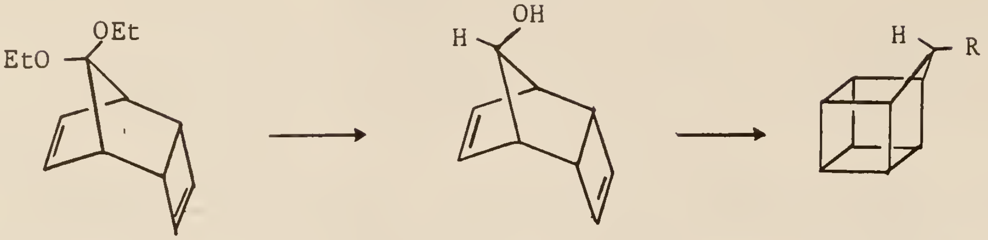


75 76 77

a, X=CO_2H
b, X=H

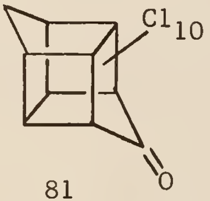
Recently the degenerate 9-homocubyl cation has been investigated by two sets of workers[8,88]. The synthesis reported by Barborak and Pettit[8] is the simpler of the two. Oxidative decomposition of cyclobutadieneiron tricarbonyl (24) with lead tetraacetate in pyridine in the presence of cyclopentadienone diethyl ketal afforded adduct 78. Hydrolysis of this compound followed by reduction with sodium borohydride gave predominately the alcohol 79. Irradiation of 79 yielded homocubanol 80a.

Schleyer[88] had reported that the acetolysis rate of 80b was 3.38 ± 0.09 x 10^{-4} sec^{-1} at 100°, and that solvolysis in unbuffered formic acid at reflux allowed complete degeneracy of the 9-homocubyl cation to be achieved.

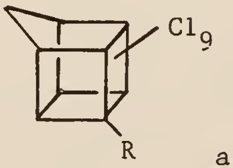


78 79 80 a, R=OH
b, R=OTs

Nonachloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-4-carboxylic acid (82a) may be prepared in 80-90% yield by the Favorskii rearrangement of decachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decan-10-one (81)[84]. A series of compounds with structure 82 was prepared, including the amine 82b. This compound's most striking property is its great sensitivity to base. It is destroyed almost instantly by 0.01 N hydroxide ion in homogenous solution. It was also reported that 82b was deaminated smoothly and rapidly by treatment with nitrous acid or nitrosyl chloride near room temperature, but the products obtained were those expected from attack of an intermediate bridge-head radical on the solvent or reagent[85].

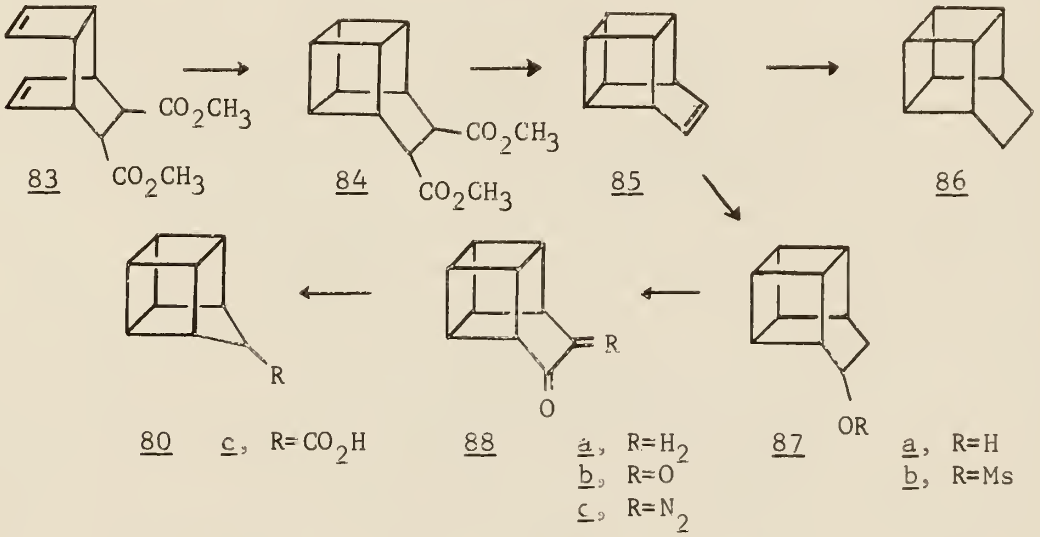


81

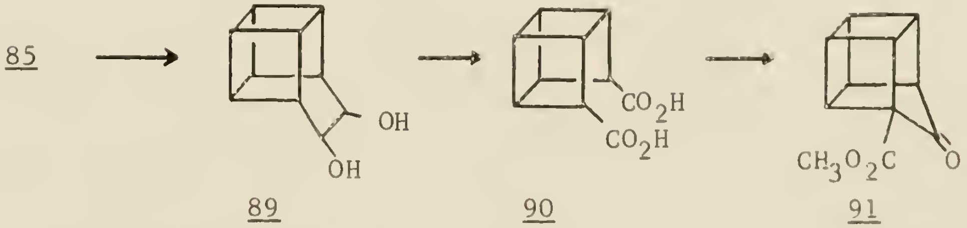


82 a, R=CO_2H
b, R=NH_2

Both the saturated (86) and unsaturated (85) 1,1'-bishomocubyl systems have been prepared by several workers[28,37,58,83]. The method used by Dauben and Whalen[28] involved the acetone photosensitized reaction of diester 83 to give the photocyclic isomer 84. Hydrolysis of this compound with potassium hydroxide in methanol yielded the trans-photodiacid which was bisdecarboxylated to give pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene (85). Hydrogenation of olefin 85 with prereduced platinum oxide yielded the parent saturated hydrocarbon 86. Hydroboration of olefin 85 yielded alcohol 87a, which was oxidized by the Jones procedure to ketone 88a. Selenium dioxide oxidation of this ketone yielded the diketone 88b, which was converted to the diazoketone 88c *via* the monotosylhydrazone. Irradiation of 88c in aqueous tetrahydrofuran gave the ring contracted homocubanecarboxylic acid 80c.

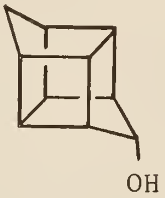

CO_2CH_3
CO_2CH_3
83
CO_2CH_3
CO_2CH_3
84
85
86
R
80
c, R=CO_2H
R
O
88
a, R=H_2
b, R=O
c, R=N_2
OR
87
a, R=H
b, R=Ms

Chin, Cuts, and Masamune[18] started with bishomocubyl olefin 85 and oxidized it to dialcohol 89. This compound was oxidized further to diacid 90, converted to the corresponding diester and reacted with methylsulfinyl carbanion to give ketone 91.

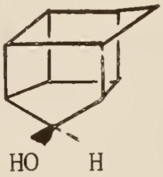

85
OH
OH
89
CO_2H
CO_2H
90
CH_3O_2C
O
91

The solvolysis of 1,1'-bishomocubyl system 87b in unbuffered acetic acid yielded a mixture of acetates which was hydrolyzed[29]. The mixture of alcohols was found to possess the following composition: 87a (10%), 92

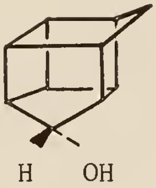
(14%), 93a + 93b (18%), 94 (2%), and 95 (56%). The fact that the major solvolysis alcohol 95 possesses the more hindered *endo* configuration indicates that the course of the reaction does not proceed entirely through classical intermediates in which the attack of solvent from the less hindered side would lead to the *exo* isomer of 95.



92

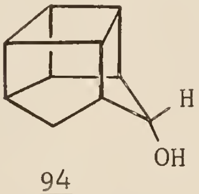


93a

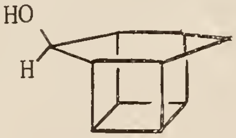


93b

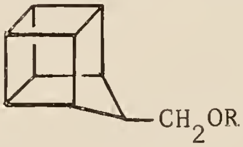
Hydride reduction of homocubanecarboxylic acid 80c afforded 96a, and its *p*-toluenesulfonate 96b was solvolyzed in buffered acetic acid. The resulting acetates were hydrolyzed and the mixture of alcohols had the following composition: 96a (52%), 92 (10%), 93a + 93b (15%), 94 (trace), and 95 (23%). The general pattern of the reaction of 96b is similar to that found for 87b, except that the major solvolysis product resulted from displacement without rearrangement.



94

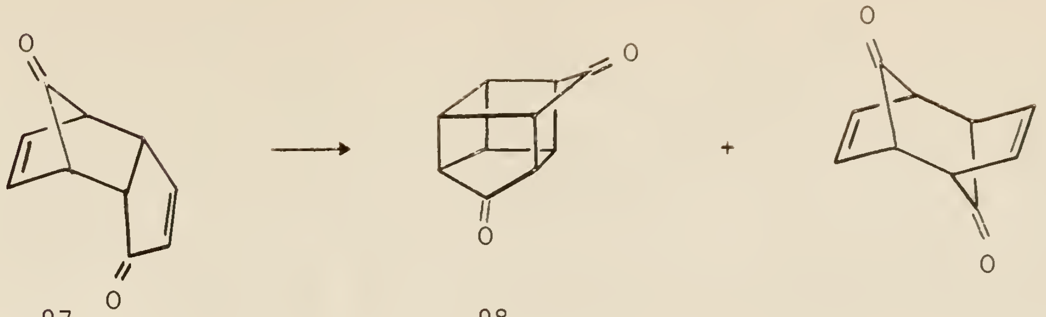


95



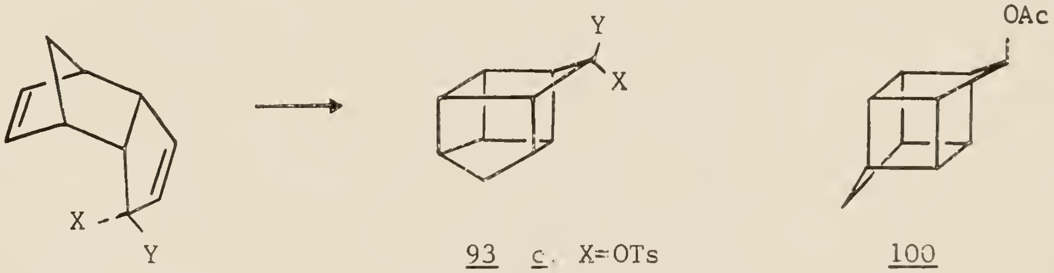
96 a, R=H
b, R=Ts

Baggiolini et al.[4] observed the photochemical reaction of diketone 97. Two products were formed with cage structure 98 being the major product.



97 98

The synthesis and solvolysis of the syn- and anti-alcohol 93a and 93b were reported by Dilling and Reineke[32] in 1967. The syn-alcohol 93a was prepared by the acetone photosensitized ring closure of endo,syn-tricyclo-$[5.2.1.0^{2,6}]$deca-3,8-dien-2-ol (99a). The tosylates 93c and 93d were prepared and solvolyzed in unbuffered acetic acid. The rate data obtained at 120° was $2.84 \pm 0.12 \times 10^{-4}$ sec^{-1} for 93c and $4.90 \pm 0.22 \times 10^{-5}$ sec^{-1} for 93d. The major product acetates, 93e and 100 were rationalized as arising via 1,2-alkyl shifts and by substitution with retention of configuration.



99 a, X=OH
b, Y=OH

93 c, X=OTs
d, Y=OTs
e, Y=OAc

100

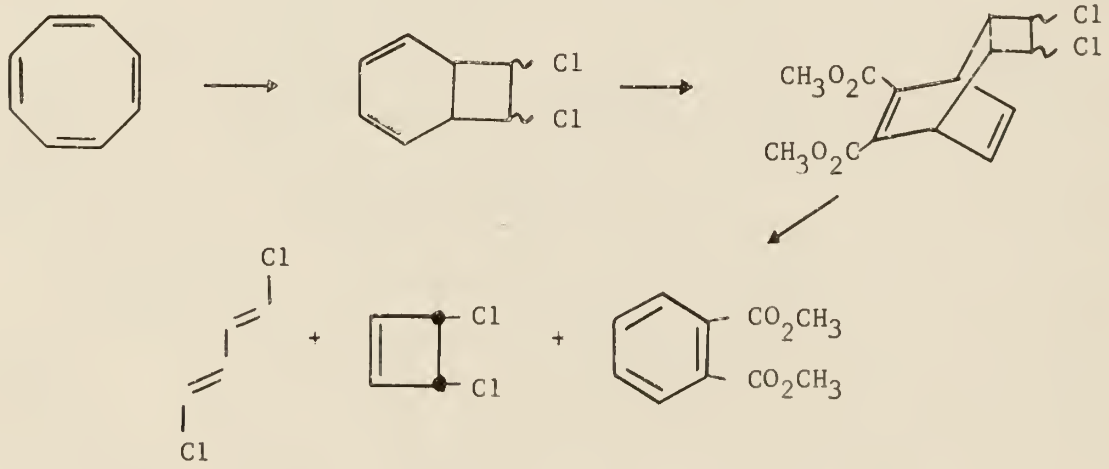
OBJECTIVES OF THIS INVESTIGATION

The objectives of this investigation are:

1. To synthesize endo-bicyclo[2.2.0]hex-2-yl acetate and certain of its precursors.
2. To study the effect of ring strain on the reactions of some simply substituted bicyclo[2.2.0]hexanes.

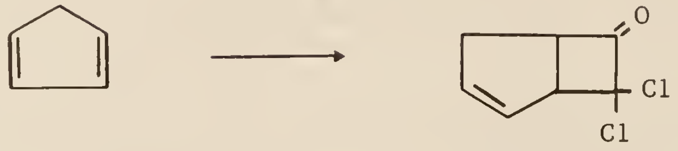
DISCUSSION OF EXPERIMENTAL RESULTS

At the time this work began, no simply substituted *endo*-bicyclo[2.2.0]-hexane derivatives had been reported. Therefore, a study was initiated to find a synthetic method which was applicable to preparative work in this area. A convenient starting material was judged to be *cis*-3,4-dichloro-cyclobutene (*101*), and synthesis by a known sequence of reactions made this compound easily available[1]. The free radical chlorination of cyclooctatetraene produces a mixture of *cis*- and *trans*-7,8-dichlorobicyclo[4.2.0]-octa-2,4-diene, with the *cis* isomer present in a ratio of approximately 4:1 over the *trans*. Diels-Alder reaction of this mixture with dimethyl acetylenedicarboxylate followed by a retro-Diels-Alder reaction produces a mixture of cyclobutene *101* and *trans*,*trans*-1,4-dichlorobutadiene (*102*). The butadiene *102* arises from ring opening of the *trans*-chlorinated product during pyrolysis[36].



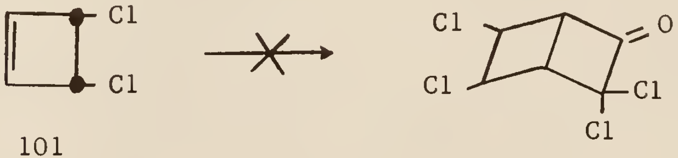
102 *101*

It was considered that a cycloaddition reaction between *101* and a ketene might provide entry into the bicyclo[2.2.0]hexane system. Stevens and co-workers[100] had reported the cycloaddition reaction of cyclopentadiene with dichloroketene at 0° gave the unsaturated bicycloketone 103 in 70% yield.



103

The analogous reaction with cyclobutene 101 was attempted under various conditions and relative concentrations, but none of the anticipated bicyclic ketone was obtained. In all cases the starting cyclobutene was recovered along with a polymeric material attributed to the dichloroketene. In these

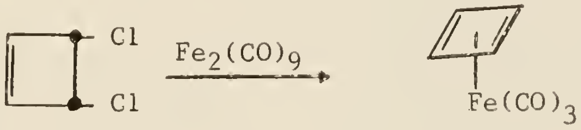


101

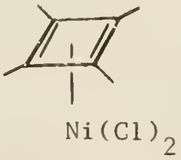
attempts the dichloroketene was prepared *in situ*. A method is available for isolating the ketene in a hydrocarbon solvent where it is stable for approximately a week at 5°[11]. It might be profitable to continue this attempt using isolated dichloroketene. If the reaction did go, it is doubtful if the desired product could be isolated, due to the facile rearrangement of bicyclo[2.2.0]hexan-2-one[62].

The above reaction was not investigated further, and attention was turned to the use of cyclobutadiene. Early in 1965, Pettit and co-workers[36] published the synthesis of cyclobutadieneiron tricarbonyl (24) from *cis*-3,4-dichlorocyclobutene (101). The reported conditions were to allow 101 and an excess of diiron enneacarbonyl in pentane to react for 2 hours at 30°, resulting in a 40% yield of complex 24. In our hands, none of the desired complex 24 could be obtained using these conditions. The starting cyclobutene was always recovered along with 60% of the initial enneacarbonyl. This loss of enneacarbonyl was attributed to the formation of a complex with the cyclobutene which decomposed on removal of the solvent. The infrared spectrum of the crude reaction mixture gave absorptions at 4.94 and 5.10 μ plus all the correct absorptions for 101. Removal of the solvent left only the peaks of 101. Alkeneiron carbonyl complexes are known and are found to be unstable toward temperature, moisture, and oxygen[69].

It was then decided to try and force the reaction by employing conditions similar to those Criegee and Schroder[24] used in 1959 to prepare tetramethylcyclobutadienenickel dichloride (104) from tetramethyldichlorocyclobutene and nickel tetracarbonyl. These conditions called for a much higher bath temperature (60°) and a longer reaction time (50 hrs.) under a nitrogen atmosphere. Using these conditions a 10% yield of 24 was obtained. From this starting point and adjusting to optimum conditions, a consistent 48% yield of complex 24 with no recoverable starting materials was realized. The use of less than a 40% excess of diiron enneacarbonyl results in a lower yield of complex 24 and the recovery of some unreacted cyclobutene 101.



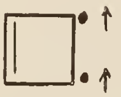
101 24



104

The complexed cyclobutadiene 24 has been shown to be aromatic in the sense that it undergoes electrophilic substitution reactions to yield a series of new cyclobutadiene complexes[38]. These reactions find a close parallel with the well-known substitution reactions of ferrocene.

The first experiment which claimed to provide an answer to the question of the electronic structure of cyclobutadiene involved the reaction of 3,4-dichlorotetramethylcyclobutene with sodium-potassium vapors at 250°. On the basis of the nature of the organic products produced in this reaction, Skell and Peterson[93] deduced that cyclobutadiene possessed a triplet ground state (105), a result which was in accord with the prediction from earlier theory[74]. However, this conclusion can be questioned on the grounds of the nature of the experimental conditions employed in the reaction; for example, if free tetramethylcyclobutadiene is involved, then reaction *via* thermally produced triplet excited species is readily conceivable[108].



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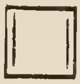

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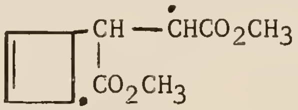

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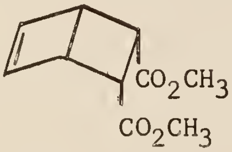

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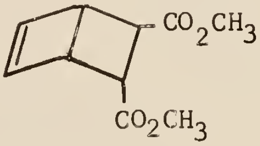
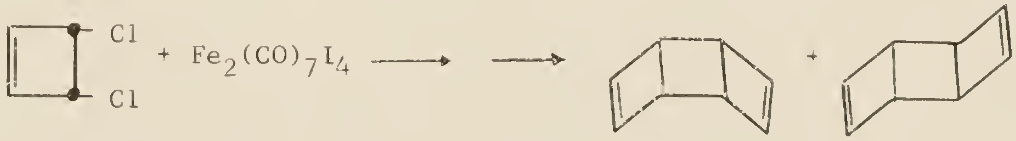


26

Watts, Fitzpatrick, and Pettit[108] decomposed complex 24 in the presence of dimethyl maleate to obtain *cis*-diester 25, and in the presence of dimethyl fumarate to obtain *trans*-diester 26. The stereochemistry of the adducts 25 and 26 are just those one would expect if cyclobutadiene were to act as a singlet diene (106) in the normal Diels-Alder reaction. Stereospecific addition would not be expected to occur if cyclobutadiene was a triplet. In such an event the addition to both dimethyl maleate and dimethyl fumarate should be a two-step process involving the common triplet species 107. Following the work of Pettit[108], the self-consistent field molecular orbital calculations for cyclobutadiene were done by Dewar and Gleicher[31]. Their results also suggest that the ground state of cyclobutadiene is a singlet (106) rather than a triplet (105). An experiment has been done showing that free cyclobutadiene is liberated from the decomposition of complex 24[107].

Another method of preparing cyclobutadieneiron tricarbonyl (24) was investigated prior to duplicating the conditions of Criegee. It is known that halogens facilitate the partial decomposition of diiron enneacarbonyl with formation of a complex with the formula $Fe_2(CO)_7X_4$; where X can be chlorine, bromine, or iodine[46]. As demonstrated by Hieber[46], this complex can act as a halogenating agent. Formation of this complex and reaction with cis-3,4-dichlorocyclobutene (101) produced a product mixture that could not be separated by column chromatography on alumina or thin-layer chromatography on silica gel. The products identified from vapor phase analysis (g.c.) were syn- (56) and anti-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (57), present in the ratio of 2:3. These products were not present before

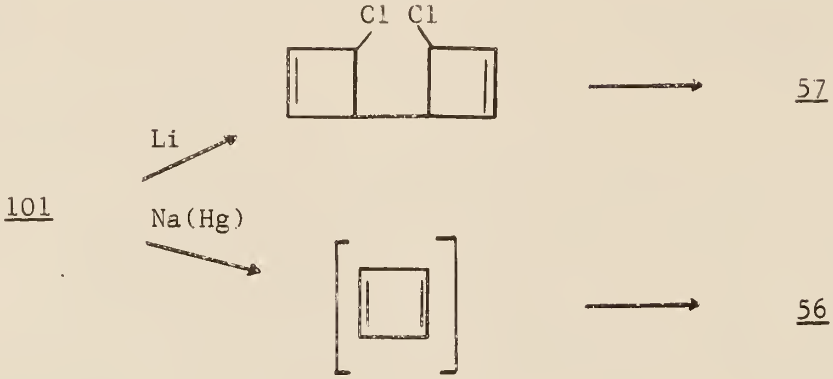


101

56

57

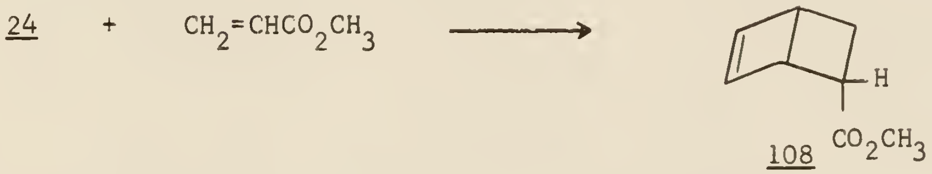
g.c. collection as shown by infrared spectral comparisons. The process by which the dimers of cyclobutadiene were formed is not known, but it is assumed that no free cyclobutadiene was involved. Pettit et al.[108] found that liberation of free cyclobutadiene from complex 24 resulted in a syn to anti ratio of approximately 5.1. Nenitzescu and co-workers[2] found that cyclobutene 101 reacted with sodium amalgam to give free cyclobutadiene which dimerized to *syn* isomer 56. Reaction of 101 with lithium produced a step-wise dimerization to give *anti* isomer 57.



After preparing dimethyl bicyclo[2.2.0]hexa-2,5-diene-2,3-dicarboxylate (37) for comparison with that prepared by Watts, Fitzpatrick and Pettit[107], the possibility of cyclobutadiene reacting with certain monosubstituted olefins was investigated. The ones considered were: vinyl acetate, 2-butenone, and methyl acrylate. Each olefin was subjected to the reaction conditions because of the well known ability of ceric ion to oxidize a wide variety of organic compounds[73].

It was found that 2-butenone was unstable in the presence of ceric ion and was immediately oxidized to a polymeric material. Vinyl acetate, although the most stable of these olefinic compounds to ceric ion, would not react with the cyclobutadiene. In all attempts, the reaction mixture on vapor phase chromatography yielded only unreacted vinyl acetate and a polymeric material. No reason can be given for the failure of this reaction. An answer will not be possible until more dienophiles have been allowed to react with cyclobutadiene.

Methyl acrylate was intermediate between 2-butenone and vinyl acetate in its stability toward ceric ion. Cyclobutadiene reacted with methyl acrylate to produce a mixture of products, which on column chromatography yielded a material in 3% yield with n.m.r. absorptions consistent with the methyl endo-bicyclo[2.2.0]hex-5-ene-2-carboxylate (108) structure. The



108

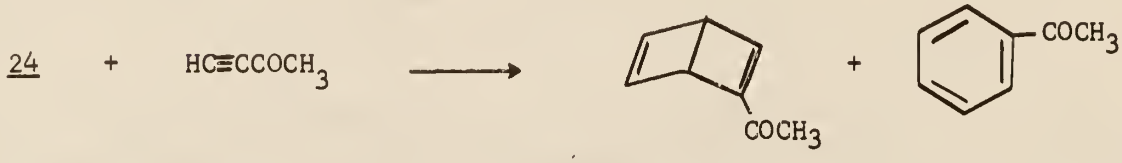
analogy with other Diels-Alder reactions and the work of Pettit and co-workers[107] in the reaction of cyclobutadiene with dimethyl maleate giving exclusively endo isomer 25 lend further strength to this assignment. endo-Ester 108 was catalytically reduced in 50% yield to a mixture of three products. No conclusive spectral data could be obtained on the reaction product. This procedure was then discontinued as a means of getting into the bicyclo[2.2.0]hexyl system due to the extremely low yield of the Diels-Alder reaction and the inconclusive information from the reduction.

Attention then turned to the use of acetylenic compounds for reaction with cyclobutadiene. Pettit and co-workers[107] had reported the successful use of several monosubstituted acetylenic compounds. Not mentioned among the list was 2-butynone (109), judged to be the best compound for gaining quick entry into the simply substituted endo-bicyclo[2.2.0]hexanes. Although several procedures are available for preparing substituted acetylenic methyl ketones[52,67,106], no good method is available for preparing the parent compound. The procedure decided upon produced the desired ketone in 9% yield[52,92].

$$\text{H-C}\equiv\text{C-H} + \text{EtMgBr} \longrightarrow \text{H-C}\equiv\text{C-MgBr} \longrightarrow \text{H-C}\equiv\text{C-COCH}_3$$

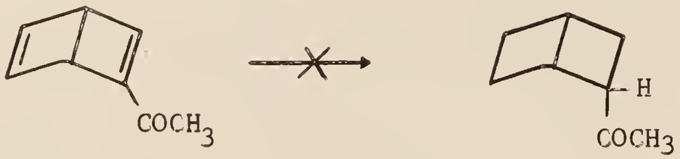
109

Reaction of 2-butynone (109) with cyclobutadieneiron tricarbonyl (24) and ceric ion resulted in the formation of bicyclo[2.2.0]hexa-2,5-dien-2-yl methyl ketone (110) and aromatic isomer 111 in 27% yield. The n.m.r. spectrum (page 59) of 110 showed absorptions similar to those reported for



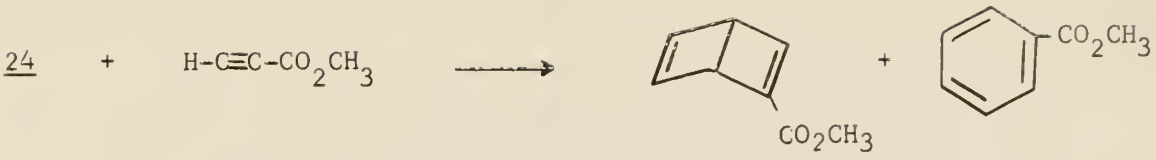
109 110 111

methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (114)[107]. Injection into a g.c. at a detector temperature of 304° resulted in quantitative isomerization of 110 to the aromatic isomer 111. No other detector temperatures were investigated. Three attempts at diimide reduction of structure 110 to the saturated endo-bicyclo[2.2.0]hex-2-yl methyl ketone (112) met with complete failure[102]. In each case, g.c. analysis of the product mixture showed thirteen components to be present. The only identifiable compound was acetophenone (111) which had been present in the synthesis of 110. This reaction was not investigated further and, therefore, no information is available as to what caused the decomposition of diene 110 or the nature of the other twelve products.



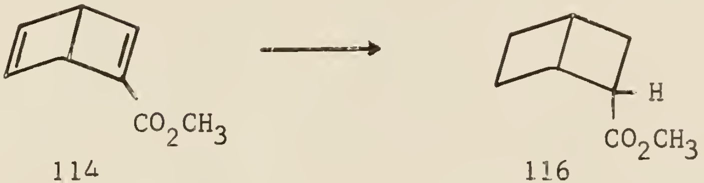
110 112

Watts, Fitzpatrick, and Pettit[107] had reported the preparation of methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (114) from the reaction of cyclobutadiene with methyl propiolate (113). Duplication of this



113 114 115

reaction resulted in a 63% yield of diene 114 and methyl benzoate (115). The n.m.r. spectrum (page 59) of ester 114 agreed with that reported[107]. Injection into a g.c. at a detector temperature of 304° (the only



114 116

temperature investigated) resulted in quantitative isomerization of "Dewar benzene" 114 to the aromatic isomer 115, as did attempted catalytic hydrogenation over platinum. This same result was obtained by van Tamelen and Pappas[104] in the attempted reduction of bicyclo[2.2.0]hexa-2,5-diene (30). These authors did find that diimide, generated from the dipotassium salt of azodicarboxylic acid[102], would reduce 30 to bicyclo[2.2.0]hexane.

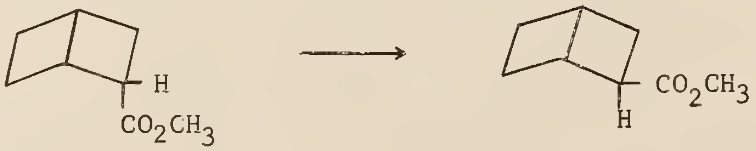
Applying this method to ester 114 gave a product in 93% yield which was assigned structure 116. The yield for this reaction is based on the n.m.r. integration of the amount of diene 114 present in the reaction mixture. This result should be good to at least ± 5% accuracy[65]. The methyl endo-bicyclo[2.2.0]hexane-2-carboxylate (116) structure was assigned to this molecule on the basis of the n.m.r. spectrum (page 61) and analogy to diimide reductions of other bicyclic olefins[42,64,103].

The mass spectrum (page 29) of ethyl endo-bicyclo[2.2.0]hexane-2-carboxylate, prepared by transesterification of the methyl ester 114 during a reduction in ethanol, showed a parent ion at m/e 154 and the 100% peak at m/e 81 corresponding to $C_6H_9^+$.

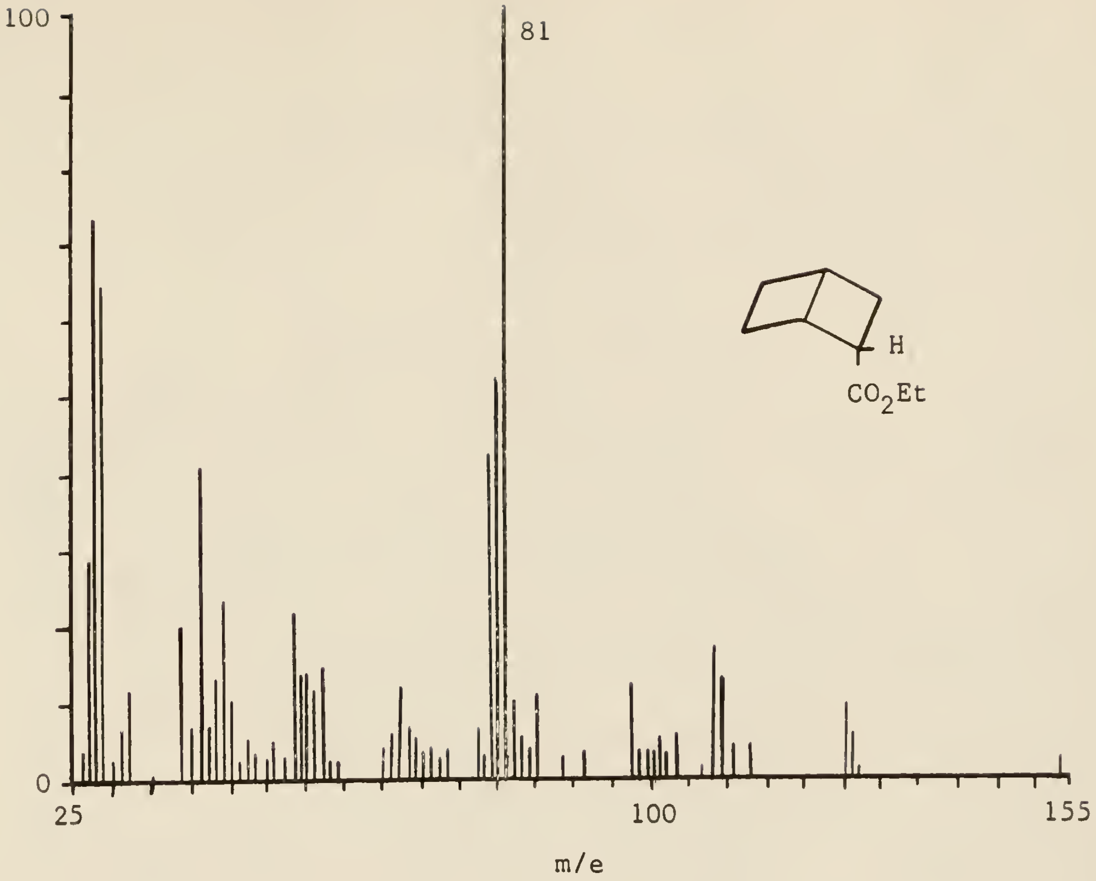
The stability of methyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate (116) toward acid and base equilibration was investigated. No epimerization occurred with the use of sodium metal in anhydrous methanol. The major product isolated from the reaction was *endo*-bicyclo[2.2.0]hexane-2-carboxylic acid (129) which was reesterified with diazomethane to 116. It is not known whether the saponification took place during the reaction or during the work-up which followed. The same results were obtained in two separate attempts. The minor product isolated in each case was unchanged ester 116.

The product isolated after acid equilibration of 116 was found to differ from the starting ester by infrared (page 49) and n.m.r. (page 61) spectra. G.c. analysis of the product showed that it had the same retention time as the starting material. The n.m.r. spectrum suggested that the bicyclo[2.2.0]hexyl system was still present and for this reason the compound was assigned the structure methyl *exo*-bicyclo[2.2.0]hexane-2-carboxylate (117). The extent of epimerization is unknown since the spectra are so near alike, and both compounds have the same g.c. retention time.

Dreiding molecular models suggest that the *endo* 2-substituted isomers of the bicyclo[2.2.0]hexyl system are much more sterically hindered than the analogous *exo* isomers. It is not surprising, then, to find that *endo* isomer 116 will epimerize to *exo*-ester 117. It has been previously observed that *exo*-bicyclo[2.2.0]hexan-2-ol (7a) would not equilibrate

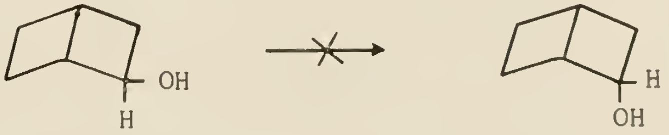


116 117



Mass spectrum of ethyl endo-bicyclo[2.2.0]hexane-2-carboxylate.

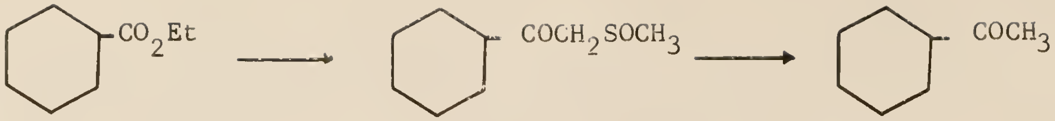
to the endo isomer (12)[62].



7a

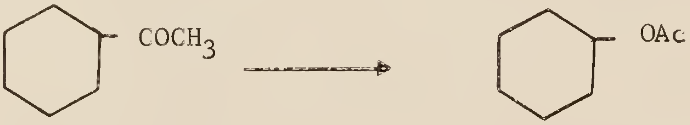
12

Reaction of methylsulfinyl carbanion with ester 116 was considered the shortest possible route to ketone 112. The reaction conditions were worked out, as previously described, with ethyl cyclohexanecarboxylate (118) to yield acetylcyclohexane (119)[22]. To complete the sequence of reactions, ketone 119 was treated with both m-chloroperbenzoic acid[114] and peracetic



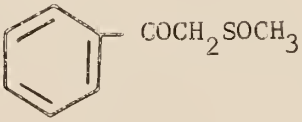
118 119

acid to produce cyclohexyl acetate (120). The reaction with m-chloroperbenzoic acid was 83% complete after two days and work-up yielded only acetate 120. After two days the peracetic acid reaction was 45% complete, and after 10 days, 83% complete. Work-up yielded a mixture of 119 and 120. Since the m-chloroperbenzoic acid was much faster and gave a cleaner reaction, it was chosen for use with bicyclo[2.2.0]hex-2-yl methyl ketone.



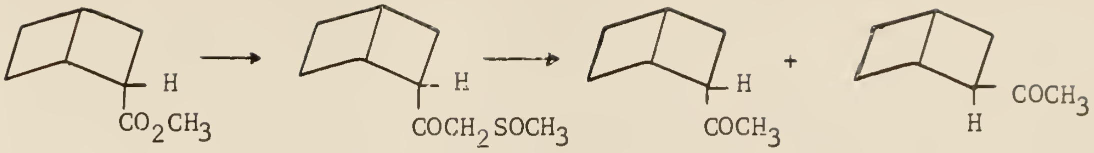
119 120

The reaction of methylsulfinyl carbanion with crude methyl endo-bicyclo[2.2.0]hexane-2-carboxylate (116), which contained some methyl benzoate (115), yielded a mixture of two adducts. A white solid removed from the mixture was identified as ω-(methylsulfinyl)acetophenone (121) by



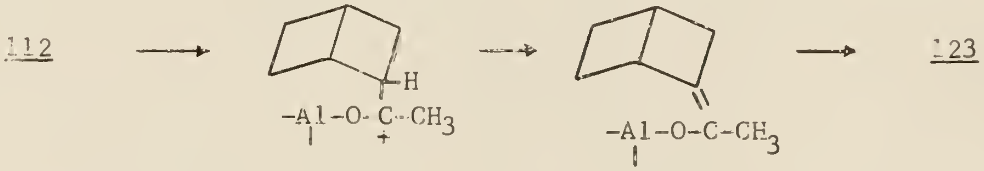
121

its n.m.r. spectrum. This compound had been previously prepared by Corey and Chaykovsky[22]. The remaining yellow oil was reduced to a mixture of ketones with aluminum amalgam. This mixture of ketones could not be separated by g.c., but the n.m.r. spectrum (page 63) integrated for a ratio of 38:62. This mixture was later identified as endo- (112) and

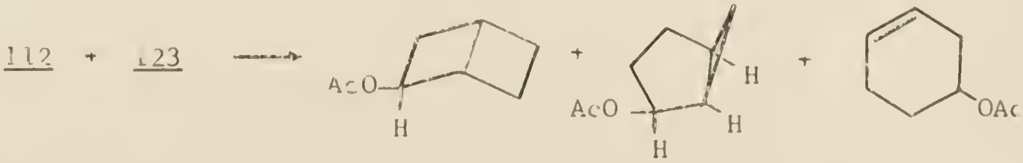


116 122 112 123

exo-bicyclo[2.2.0]hex-2-yl methyl ketone (123). The n.m.r. spectrum (page 61) of adduct 122 (n.m.r. spectrum of 121 subtracted from that of the mixture of 121 and 122) suggests only the presence of one compound. If this adduct were to isomerize to the exo isomer, it would have to go through a dianion, a situation that is not likely to occur under the reaction conditions. It is assumed, then, that the mixture of isomeric ketones arose during the reduction step. Ketone 112 could react with the aluminum hydroxide present to form a complex which would isomerize to the less sterically hindered isomer 123.



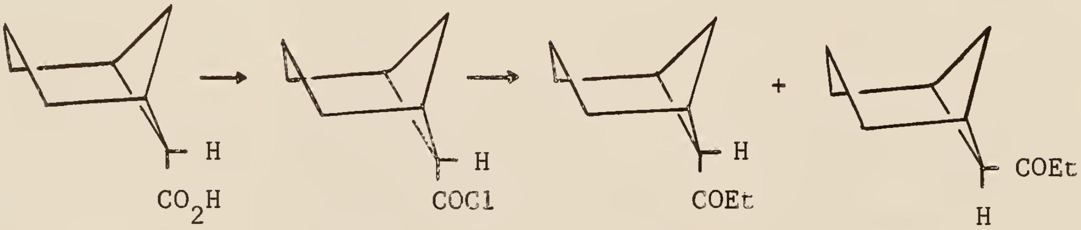
The mixture of ketones 112 and 123 was allowed to react with m-chloroperbenzoic acid for three days. The reaction mixture showed two major peaks by g.c. The major peak was identified[61] as exo-bicyclo[2.2.0]-hex-2-yl acetate (7c) and the minor one as a mixture of cis-bicyclo[3.1.0]-hex-2-yl acetate (124), 3-cyclohexenyl acetate (8), and the starting ketone mixture. The percentage of each product present was determined by a



7c 124 8

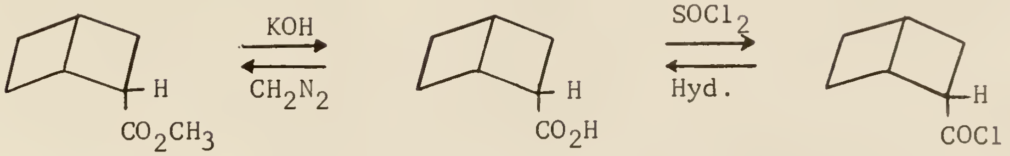
combination of n.m.r. spectral and g.c. integrations. The product mixture contained 91% of 7c, 9% of 124, and less than 1% of 8. The identification of products and a possible mechanism for their formation will be discussed later.

Since no *endo*-bicyclo[2.2.0]hex-2-yl acetate had been formed in the above mentioned reaction, the classical method of converting an ester to a ketone was investigated. Wiberg and Hess[114] had performed a similar conversion on the 6-substituted bicyclo[3.1.0]heptane system and had experienced relatively little epimerization. Formation of acid 125 from the analogous methyl ester, and its conversion to acid chloride 126 proceeded without any detectable isomerization. Conversion to ketones 127 and 128 followed by Baeyer-Villiger oxidation to the corresponding esters gave an 80:20, *endo*:*exo* isomer ratio.



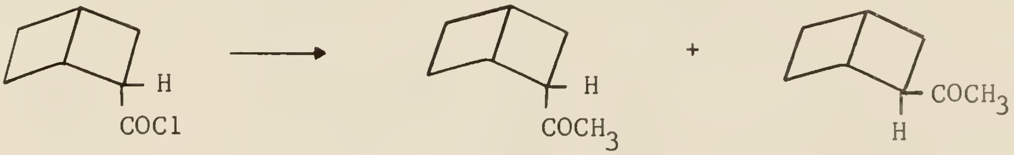
125 126 127 128

The conditions for this conversion were developed using cyclohexanecarboxylic acid. This acid was converted to cyclohexanecarbonyl chloride, and reaction with dimethyl cadmium gave acetylcyclohexane (119) in good yield. Using this same set of reaction conditions, methyl *endo*-bicyclo-[2.2.0]hexane-2-carboxylate (116) was saponified to acid 129. A small portion of this acid was reesterified with diazomethane and the resulting product was identical with 116. Acid 129 was converted to acid chloride 130, and hydrolysis gave a product which was identical with the starting material. The reaction of acid chloride 130 with dimethyl cadmium produced a mixture of ketones in low yield. The products were identified by



116 129 130

comparison with the mixture previously formed, as the endo- and exo-ketone, 112 and 123, in a ratio of 71:29, respectively. As before, this product mixture could not be separated by g.c. Since this reaction sequence

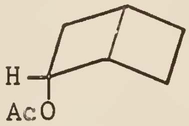


130 112 123

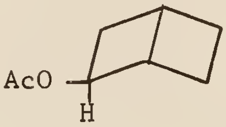
is known[113,114] to be relatively stereospecific, it can be assumed that the isomer in greater concentration is the endo isomer 112. This isomer was the one of less concentration in the reaction sequence using methylsulfinyl carbanion.

The reason that a mixture of isomers was found in this reaction sequence is probably due, in large part, to the presence of magnesium salts, which were not removed from the dimethyl cadmium. These magnesium salts could complex with the endo-ketone and allow isomerization to the more stable exo product, much in the manner previously described for the formation of this ketone mixture using methylsulfinyl carbanion. It would be of interest to see what effect pure dimethyl cadmium would have on the endo:exo isomer ratio.

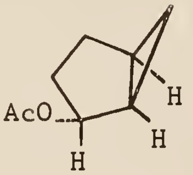
Ketones 112 and 123 were allowed to react with m-chloroperbenzoic acid for three days to produce a product mixture that showed two major peaks on g.c. These peaks were separated and the first fraction was identified as a mixture of endo- (131) and exo-bicyclo[2.2.0]hex-2-yl acetate (7c). The second fraction was a mixture of cis-bicyclo[3.1.0]hex-2-yl acetate (124) and 3-cyclohexenyl acetate (8). No starting ketones could be detected. The mixture of products contained 42% of 131, 35% of 7c, 17% of 124, and 6% of 8. The percentage of each compound present was determined by a



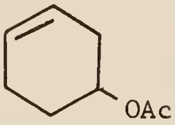
131



7c



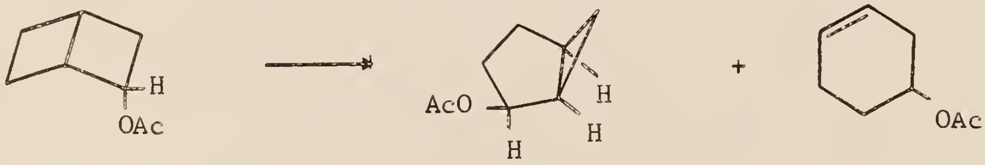
124



8

combination of n.m.r. spectral and g.c. integrations. No further separation of the products was possible. As had been previously found for some other bicyclic systems[113,114], none of the endo, exo isomer mixtures could be separated in this investigation.

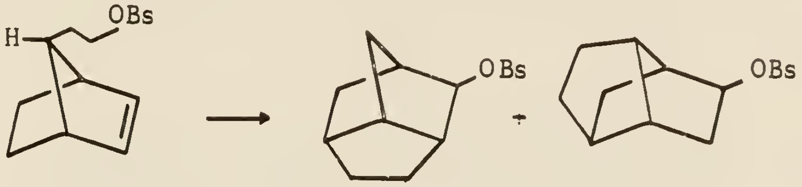
The first fraction above, containing the 54:46 ratio of 131 and 7c, was stored at −26° for 21 days in carbon tetrachloride. At the end of this period the product distribution, by n.m.r. spectral integration, had changed to 22% of 131, 46% of 7c, 25% of 124, and 7% of 8. After being



131 124 8

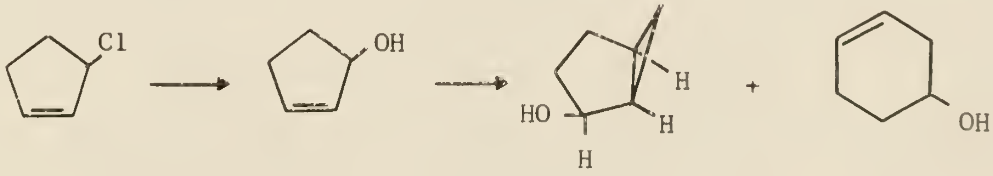
stored another 25 days in methylene chloride, the above product distribution had changed further to 14% of 131, 46% of 7c, 31% of 124, and 9% of 8. This product distribution and the stability of the products to the reaction conditions will be discussed later.

The rearrangement of a highly reactive compound in a nonpolar solvent has been previously observed[9]. Bly et al.[9] found that olefin 132 would rearrange rapidly at 33° to a mixture of 133 and 134 which in turn is converted more slowly to 133. The rearrangement took place in unbuffered carbon tetrachloride, but not in buffered solution.



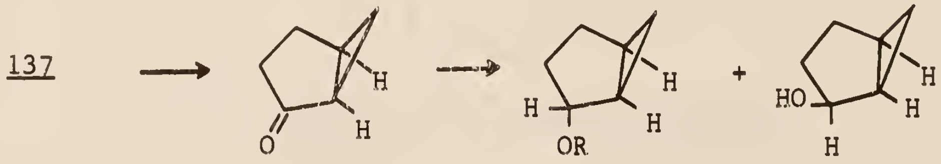
132 133 134

The proof of structure of the products obtained from the rearrangement was provided by synthesizing the compounds independently by a known set of reactions. 3-Chlorocyclopentene (135) was prepared from cyclopentadiene, and hydrolyzed to the corresponding alcohol (136)[66]. Simmons-Smith reaction of alcohol 136 yielded *cis*-bicyclo[3.1.0]hexan-2-ol (137) plus 6% of 3-cyclohexenol (138)[21,91]. The acetates prepared from these alcohols[39] were found by comparison of their n.m.r. spectra to be identical with the products, 124 and 8 from the rearrangement of 131.



135 136 137 138

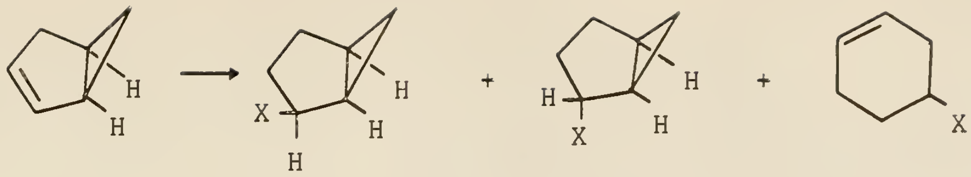
Oxidation[30] of alcohol 137 to bicyclo[3.1.0]hexan-2-one (139) followed by Meerwein-Ponndorf reduction[116] gave a mixture of two alcohols. The product consisted of an 88:12 ratio of *trans*- and *cis*-bicyclo[3.1.0]hexan-2-ol (140a and 137), respectively. Similar reduction conditions, but longer reaction time, provided Hanack and Allmendinger[44] with a 62:38 ratio of isomers 140a and 137. The longer reaction time produced the smaller amount of 140a since the thermodynamically controlled product has been shown to be 137[21]. The acetate (140b) prepared from 140a was found to be different from any of the rearrangement products.



139 140 a, R=H
b, R=Ac 137

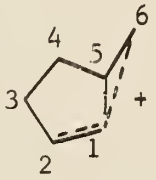
The stability of the individual products to the m-chlorobenzoic acid produced in the Baeyer-Villiger reaction was next considered. It was found that 124, 8, and 140b were all unchanged after three days exposure to the reaction conditions. exo-Bicyclo[2.2.0]hex-2-yl acetate (7c) has been previously shown to be stable under acetolysis conditions[61] and was also considered stable to these reaction conditions. Therefore, the products had to arise directly from rearrangement of endo-bicyclo[2.2.0]hex-2-yl acetate (131) and not from any of the other possible products rearranging further under the reaction conditions.

The solvolysis of cis- and trans-bicyclo[3.1.0]hex-2-yl tosylate has not been reported, but several reactions which generate the 2-carbonium ion have been performed. Freeman, Grostic, and Raymond[39] added methanol, catalyzed by p-toluenesulfonic acid, to bicyclo[3.1.0]hex-2-ene (141) and obtained three products identified as 32% of the cis isomer 142a, 53% of the trans isomer 143a, and 15% of 144a. When hydrochloric acid was added

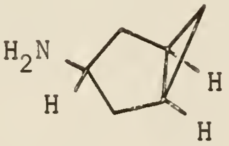


141 142 a, X=OCH_3 143 144
b, X=Cl

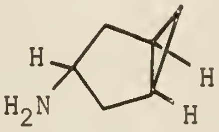
to 141, the product distribution was 31% of 142b, 66% of 143b, and 3% of 144b[40]. These authors decided that the 2-bicyclo[3.1.0]hexyl carbonium ion is similar to other substituted cyclopropylcarbinyl carbonium ions which do not rearrange under conditions of kinetic control. The greater stability of the 2-carbonium ion may be rationalized as the result of electron delocalization from the cyclopropane ring to the electron deficient C-2 as in 145.



145

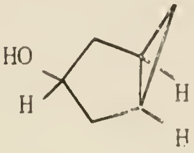


146



147

Corey and Dawson[21] found a similar situation when they examined the deamination of either cis- (146) or trans-3-bicyclo[3.1.0]hexylamine (147). In each case a mixture of four alcohols was produced. The product distribution from 146 was: 5% of 148, 30.5% of 149, 27.5% of 137, and 37% of 140a.



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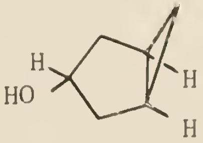
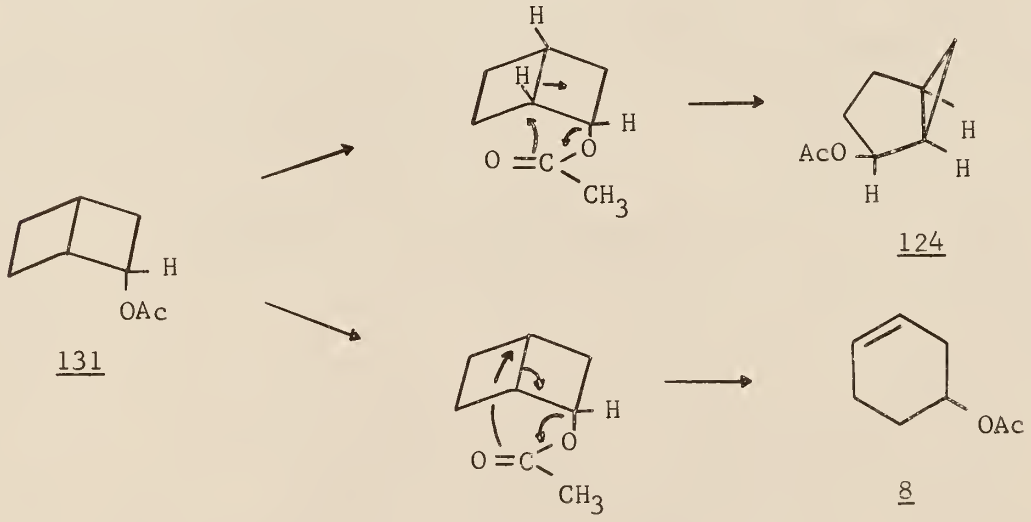


149

Amine 147 gave 41% of 148, 14% of 149, 9% of 137, and 36% of 140a. In each case where a carbonium ion was formed, a mixture of cis and trans

2-substituted products was produced, with the trans product predominating.

From the available information it appears that the rearrangement of endo-bicyclo[2.2.0]hex-2-yl acetate (131) proceeds by a concerted process to give exclusively the cis isomer 124. Since none of the products isomerize to 8 under the reaction conditions, then this compound must also arise by either a concerted process or one which incorporates a tight-ion pair. A concerted process may be questioned in this case due to the large amount of steric crowding present by attack at the C-4 position in the beginning acetate (131), as suggested by Dreiding molecular models. A study of this rearrangement using oxygen-18 labeling would be beneficial in determining if this is a completely concerted rearrangement.



131

124

8

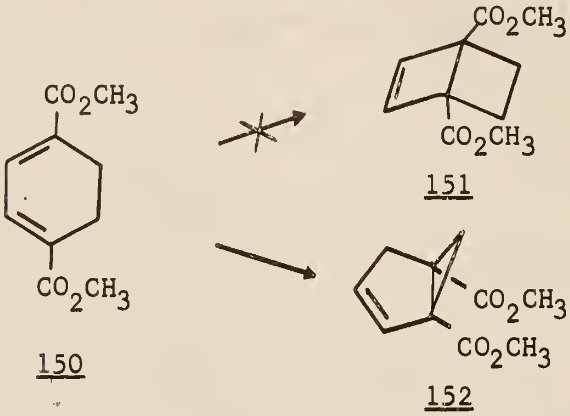
From the great difference in rates between unbuffered carbon tetrachloride and m-chlorobenzoic acid saturated methylene chloride solution, it can be assumed that the rearrangement proceeds more readily under acid catalyzed conditions. The proton from the m-chlorobenzoic acid could react with the etherial oxygen of the acetate and facilitate C_2-O bond cleavage.

The 6% increase of the exo-acetate 7c in the latter and the 29% increase in the former Baeyer-Villiger reaction can be explained by epimerization of the endo-ketone 112 to the exo-ketone 123 before reaction with the peracid. The variation in reaction conditions between the two Baeyer-Villiger reactions could explain why no endo-acetate (131) was observed in the first reaction. In this case all of the m-chlorobenzoic acid present in the peracid did not dissolve in the methylene chloride solvent, while in the second reaction all of the acid dissolved. This indicated that more acid was present in the former Baeyer-Villiger reaction.

The driving force for the rearrangement can be found in relief of steric strain arising from bond deformation of the fused cyclobutane rings. A crude calculation of strain energy can be made by summing the strain energies of the separate parts of the molecule. The calculated strain energy of cyclopropane is 31 kcal/mole[5]. Doubling this value gives 62 kcal/mole strain energy for bicyclo[1.1.0]butane. The value determined by a higher order calculation is 67.4 kcal/mole[5].

The experimentally determined strain energies of cyclopropane[5] and cyclobutane[50] are 27.5, and 26.2 kcal/mole respectively. Among the common rings, cyclohexane has a "normal" heat of combustion, but that of cyclopentane is somewhat enhanced. The Baeyer strain of the cycloalkanes is given as 24° 44' for cyclopropane, 9° 44' for cyclobutane, and 0° 44' for cyclopentane[35]. Cyclopentane can be assumed to have zero strain energy within the accuracy of this calculation. The strain energy for bicyclo[2.2.0]hexane should then be approximately twice the strain energy of cyclobutane, or 52.4 kcal/mole, and the strain energy of bicyclo[3.1.0]hexane should be equal to that of cyclopropane, or 26.2 kcal/mole. The difference in these two values is 21.4 kcal/mole. Even if this calculation is off by 5 kcal/mole, there is still a large amount of strain relief obtained by rearrangement of the bicyclo[2.2.0]hexyl system.

Before the present study was begun, a communication appeared which stated that dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (150) would react under diazomethane sensitized photolysis conditions to yield diester


CO_2CH_3
CO_2CH_3
150
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CO_2CH_3
CO_2CH_3
152

151[70]. Duplication of this work yielded only dimethyl bicyclo[3.1.0]-hex-2-ene-1,5-dicarboxylate (152). This corrected result was later published in the full paper by Prinzbach and Hagemann[71].

SUMMARY

At the time this work began, no simply substituted endo-bicyclo[2.2.0]hexane derivatives were known. A study was then initiated to find a synthetic route applicable to preparative work in this area.

The first reaction investigated was the cycloaddition reaction of cis-3,4-dichlorocyclobutene (101) with dichloroketene. This reaction was attempted under various conditions, but no anticipated bicyclohexanone could be obtained.

Reaction of diiron heptacarbonyl tetraiodide with 101 produced a non-purifiable mixture of compounds. Injection of this mixture into the g.c. produced a 2:3 ratio of syn- (56) and anti-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (57). It is assumed that no free cyclobutadiene was involved in the formation of 56 and 57.

Cyclobutadieneiron tricarbonyl (24) could not be prepared by the published procedure, but by forcing the reaction and adjusting conditions, a consistent 48% yield was obtained.

The possibility of certain monosubstituted olefinic compounds reacting with 24 was investigated. 2-Butenone was completely unstable toward the reaction conditions. Vinyl acetate, although the most stable of these olefinic compounds to ceric ion, failed to react with the cyclobutadiene. Reaction of methyl acrylate, 24, and ceric ion gave a product in 3% yield. Methyl endo-bicyclo[2.2.0]hex-5-ene-2-carboxylate (108) was assigned to this product because of the analogy with other Diels-Alder reactions run with cyclobutadiene.

Although several acetylenic compounds have been reacted with cyclobutadiene, 2-butynone (109) was not among those listed. This reaction proceeded to give bicyclo[2.2.0]hexa-2,5-dien-2-yl methyl ketone (110) and acetophenone (111) in 27% yield. Attempted diimide reduction of 110 resulted in complete destruction of the "Dewar benzene". The only identifiable compound in the complex product mixture was 111.

Methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (114) was prepared by the reaction of cyclobutadiene with methyl propiolate (113). Diimide reduction proceeded in 93% yield to produce methyl endo-bicyclo[2.2.0]-hexane-2-carboxylate (116). The endo configuration was assigned to 116 on the basis of diimide reductions of substituted bicyclo[2.2.1]heptenes.

Ester 116 was found to be stable to base equilibration attempts, but acid equilibration gave the new product, methyl exo-bicyclo[2.2.0]hexane-2-carboxylate (117). The purity of 117 is not known since the spectra of it and 116 are so nearly alike, and they have the same g.c. retention time.

The reaction of methylsulfinyl carbanion with crude 116 followed by reduction produced a 38:62 mixture of endo- (112) and exo-ketone (123).

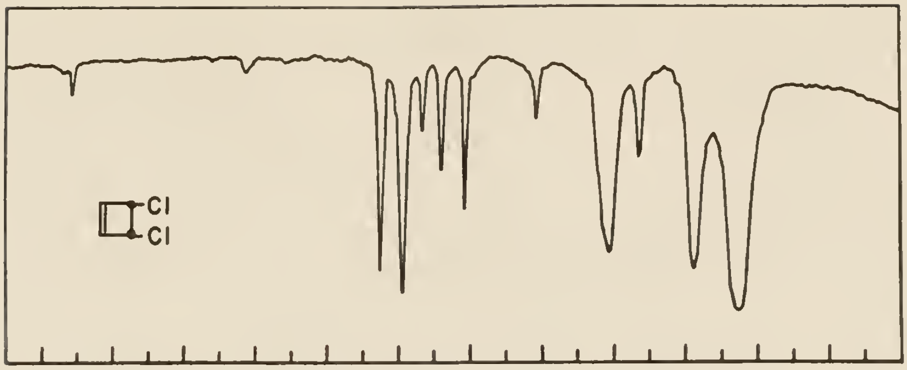
Baeyer-Villiger reaction of ketones 112 and 123 gave three products. The mixture contained 91% of exo-bicyclo[2.2.0]hex-2-yl acetate (7c), 9% of cis-bicyclo[3.1.0]hex-2-yl acetate (124), and less than 1% of 3-cyclohexenyl acetate (8). No endo-bicyclo[2.2.0]hex-2-yl acetate could be detected in the product mixture.

A second pathway to the desired compounds began with endo-ester 116 which was saponified to endo-acid 129, and 129 was converted to endo-bicyclo[2.2.0]hexane-2-carbonyl chloride (130). Neither of these two reactions gave any detectable epimerization. Reaction of 130 with dimethyl cadmium produced a 71:29 mixture of ketones 112 and 123 in low yield. Baeyer-Villiger oxidation of this ketone mixture gave four products. The product mixture contained 42% of endo-bicyclo[2.2.0]hex-2-yl acetate (131), 35% of 7c, 17% of 124, and 6% of 8.

After standing at -26° for 21 days in carbon tetrachloride, the 54:46 mixture of endo- and exo-acetate (131, 7c) had changed to 22% of 131, 46% of 7c, 25% of 124, and 7% of 8. After another 25 days in methylene chloride, the product distribution was 14% of 131, 46% of 7c, 31% of 124, and 9% of 8.

The products of the rearrangement 124, 8 and trans-acetate 140b were subjected to the Baeyer-Villiger reaction conditions and found to be stable. Therefore, the products arose directly from rearrangement of 131 and not from any of the possible products rearranging further under the reaction conditions.

It is then proposed that the rearrangement of 131 proceeds by a concerted process since no trans-acetate 140b was detected in the product mixture. In all cases where a carbonium ion is allowed to form, the major product is trans-2-substituted-bicyclo[3.1.0]hexane. The formation of 8 can also be explained by a concerted rearrangement, but steric crowding at C-4 leaves this open to question. The driving force for the rearrangement can be found in relief of steric strain.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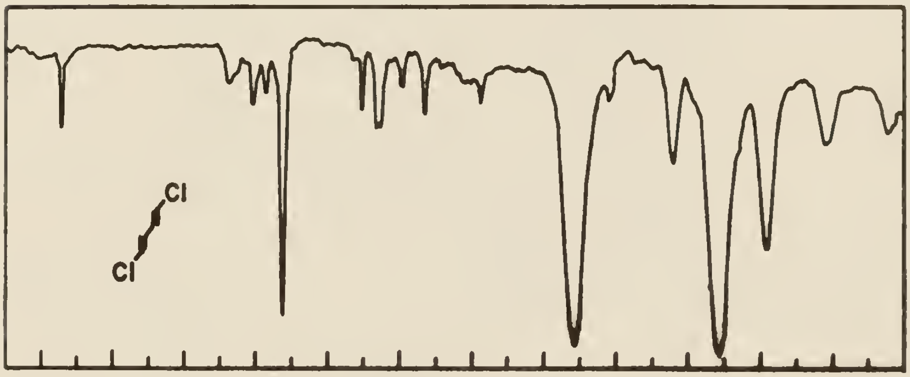
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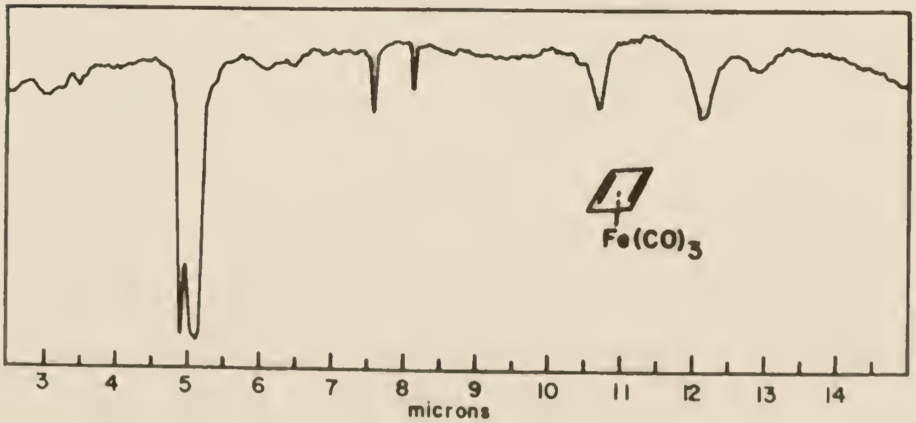
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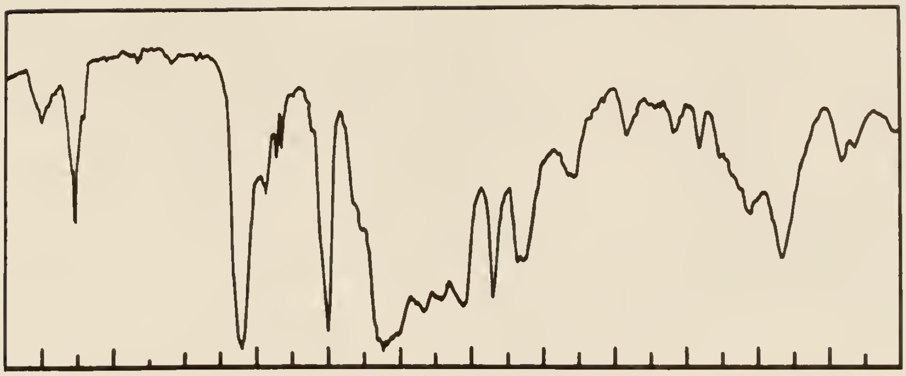

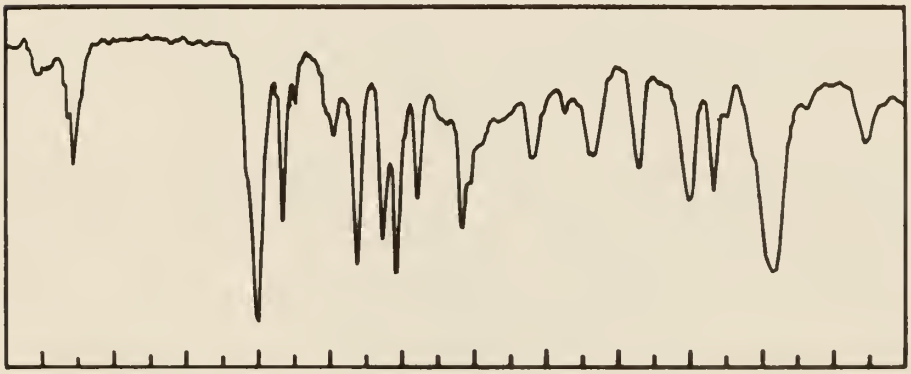

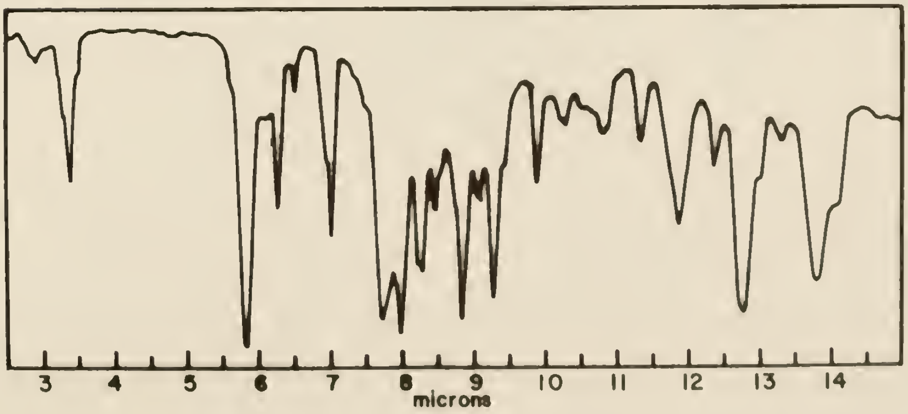
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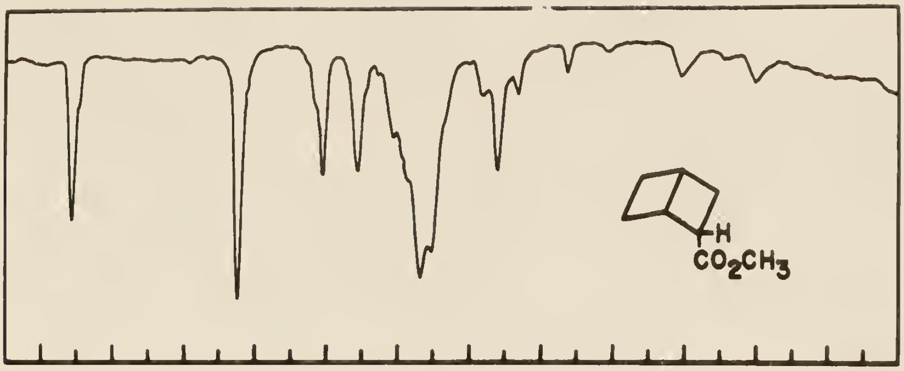
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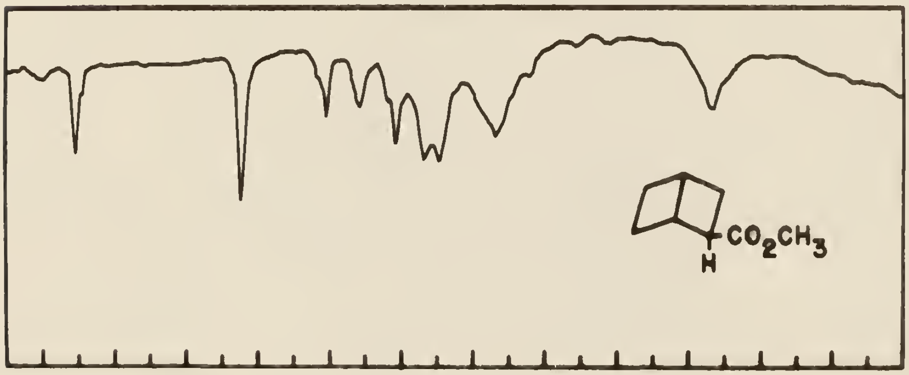
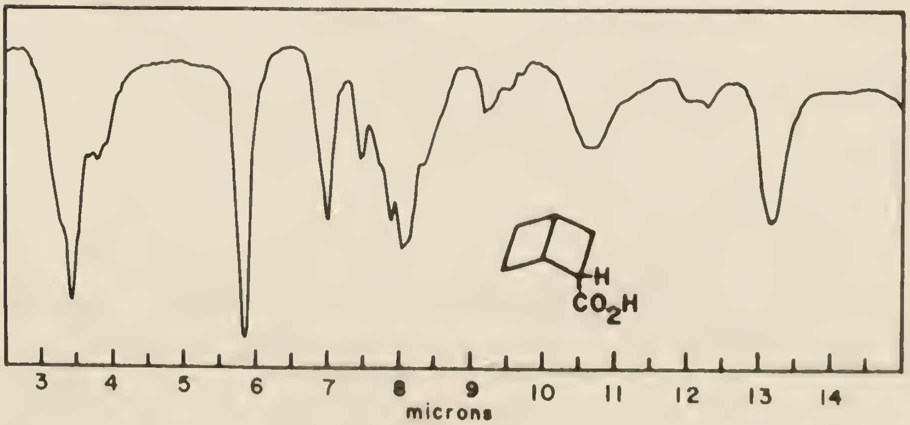

CO2CH3
H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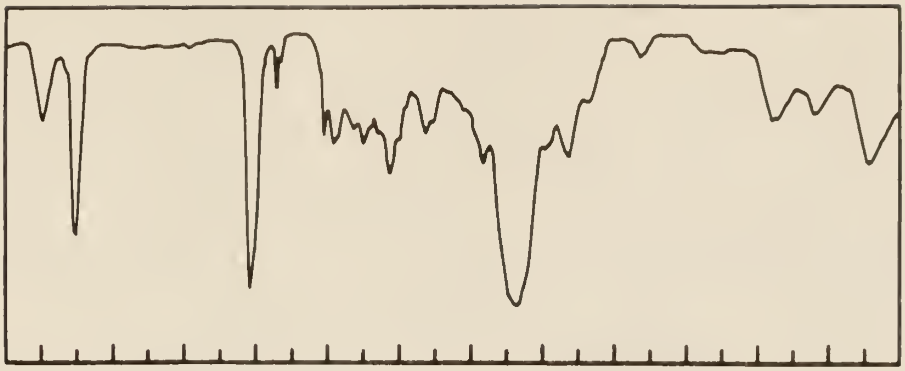

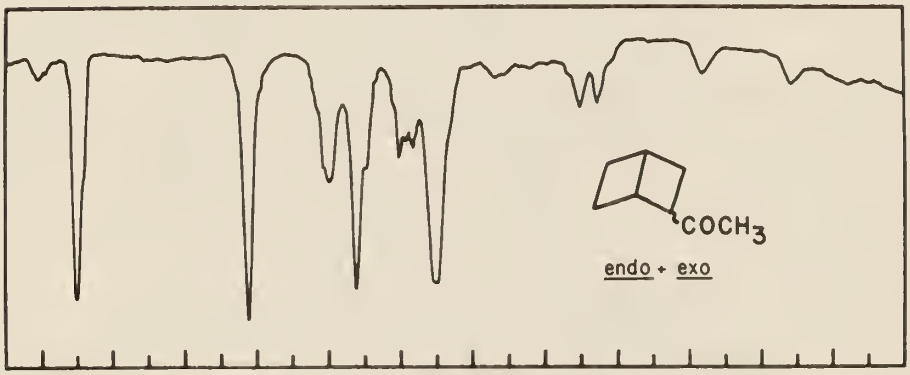
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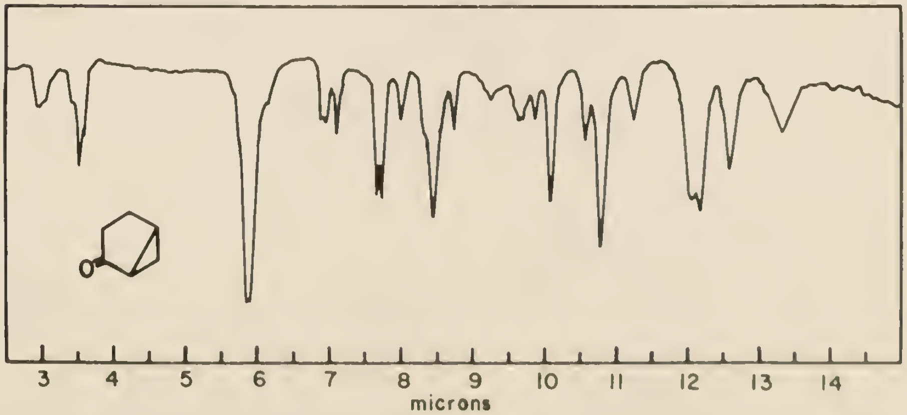
endo + exo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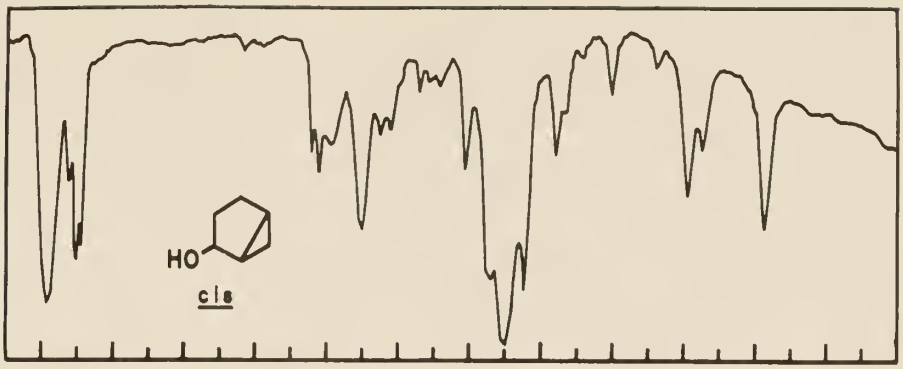
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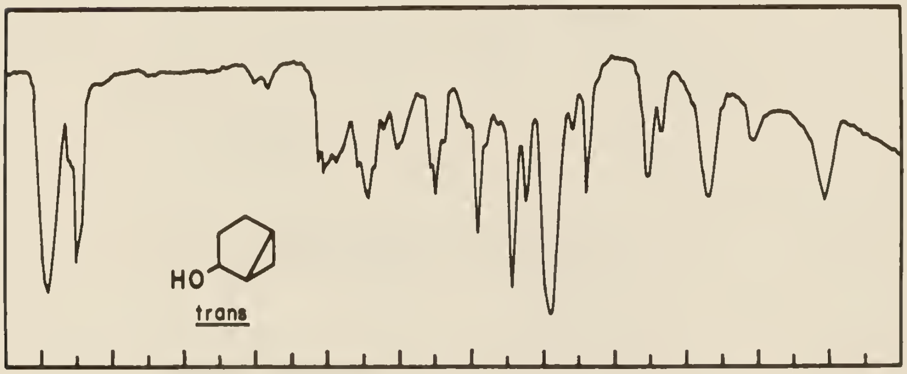
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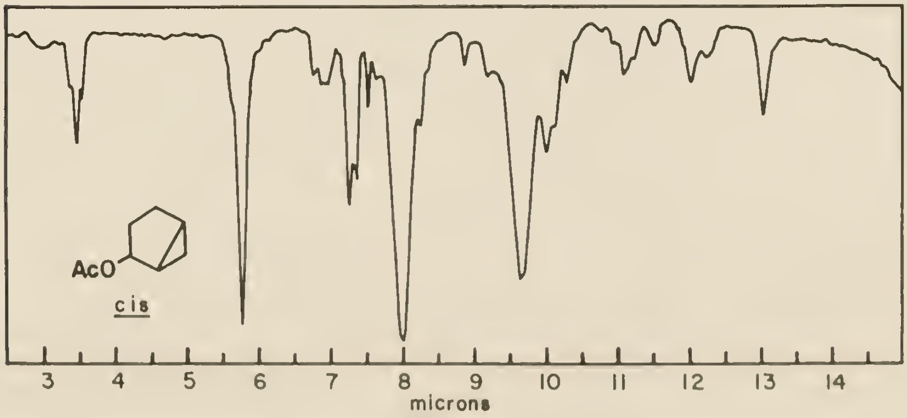
trans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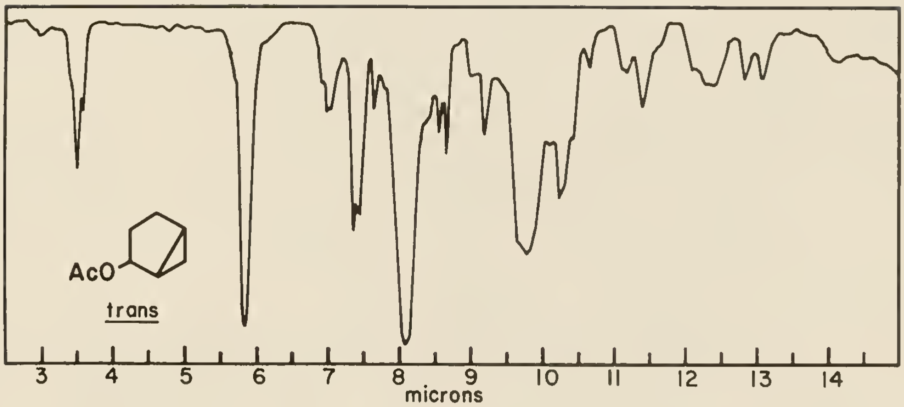
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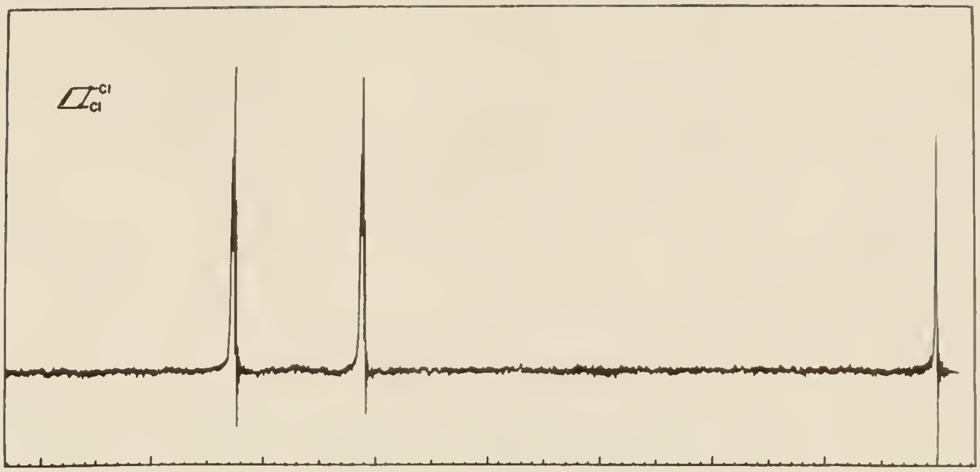
microns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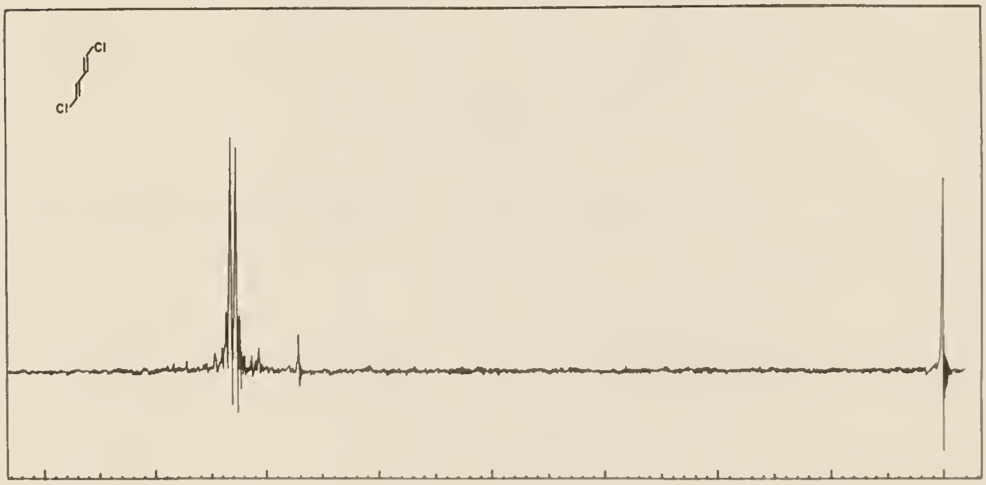
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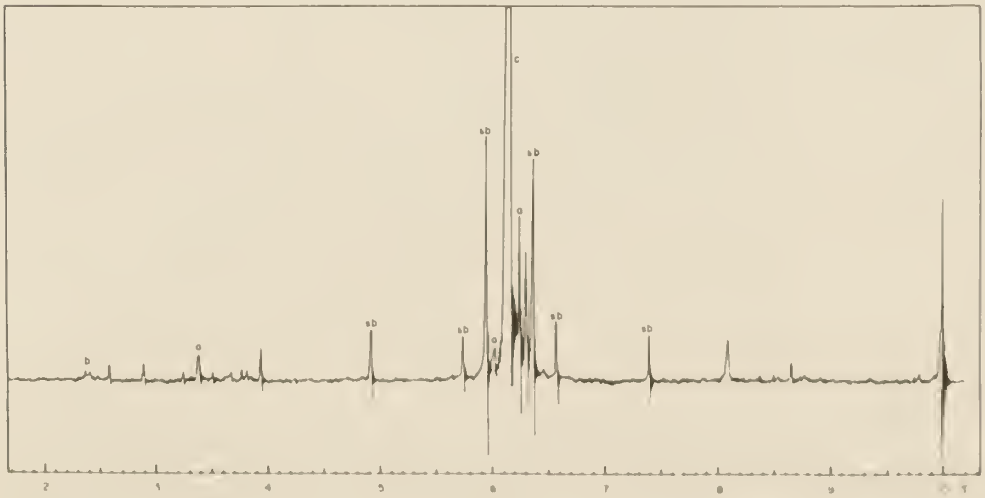
b
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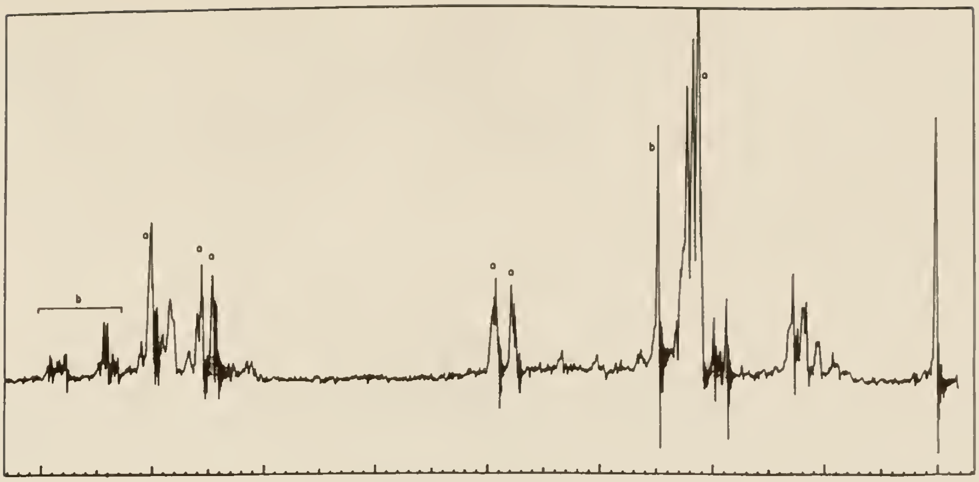
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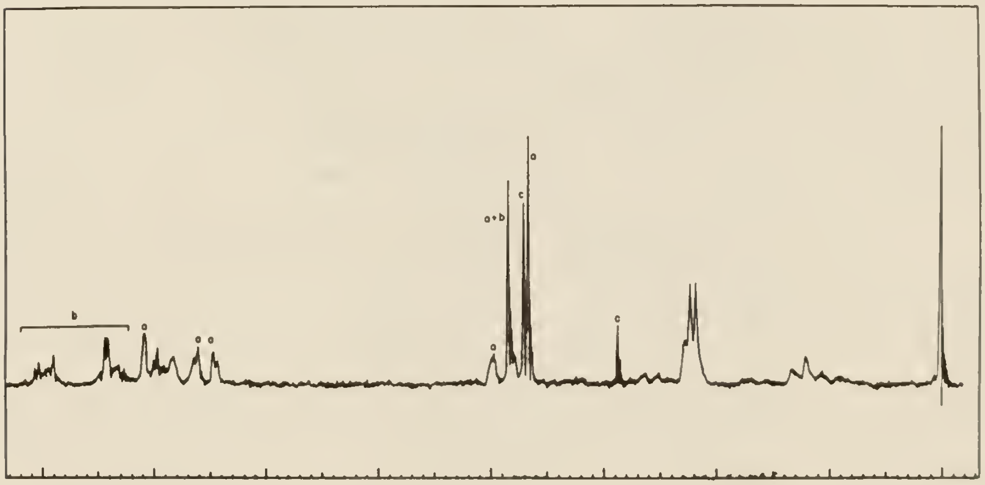
b
a


b
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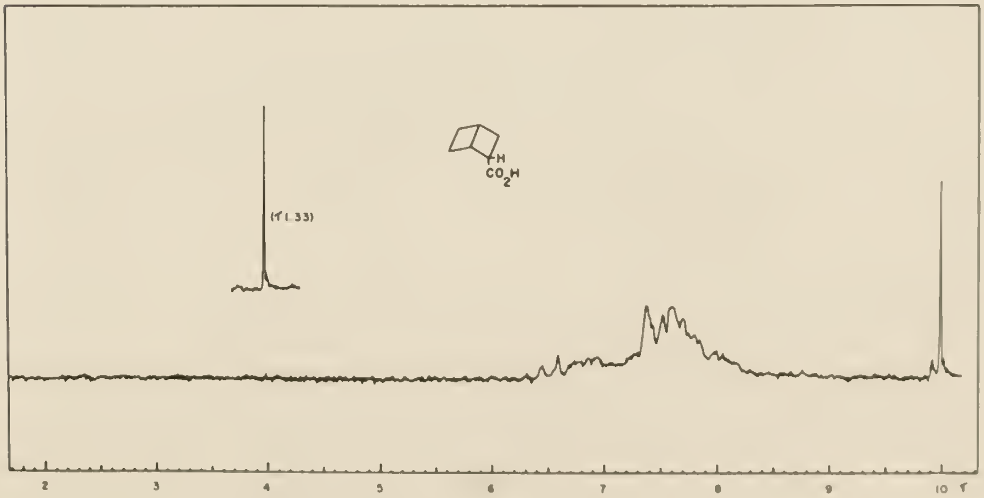
c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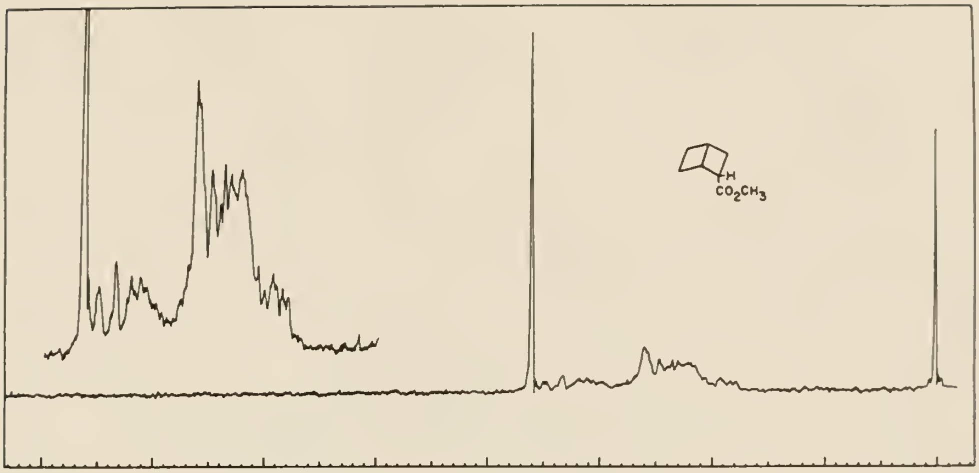
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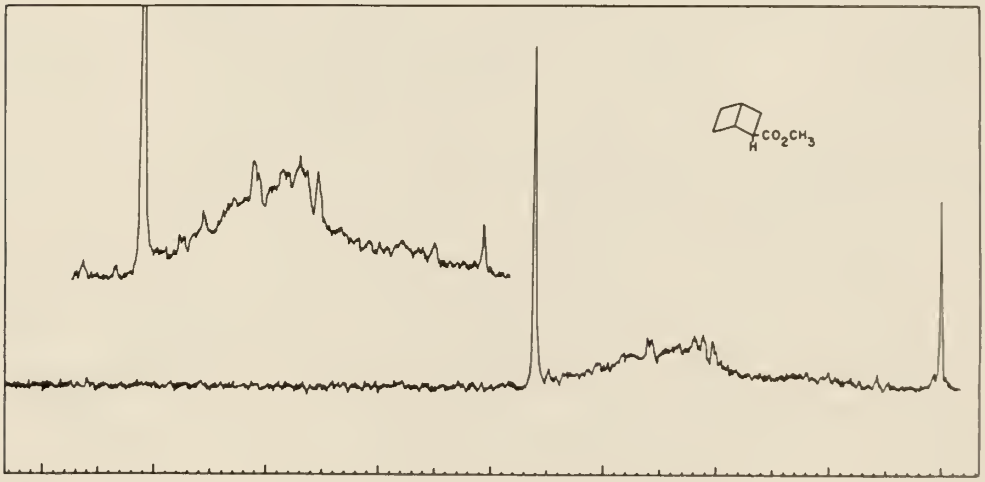
CO2CH3


CO2CH3
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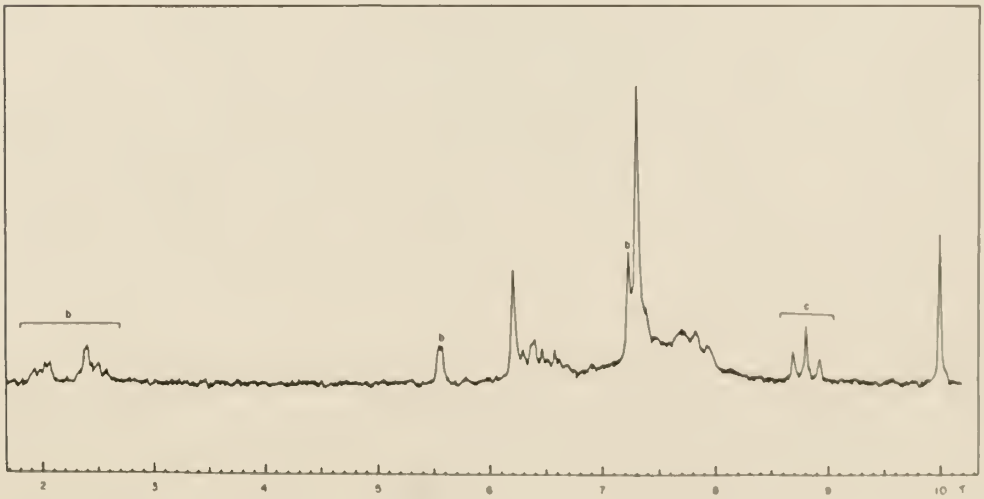
b
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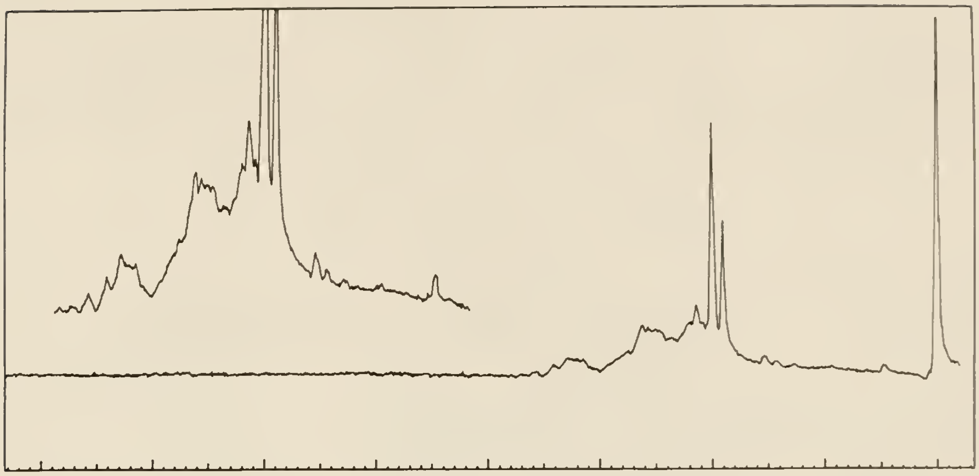

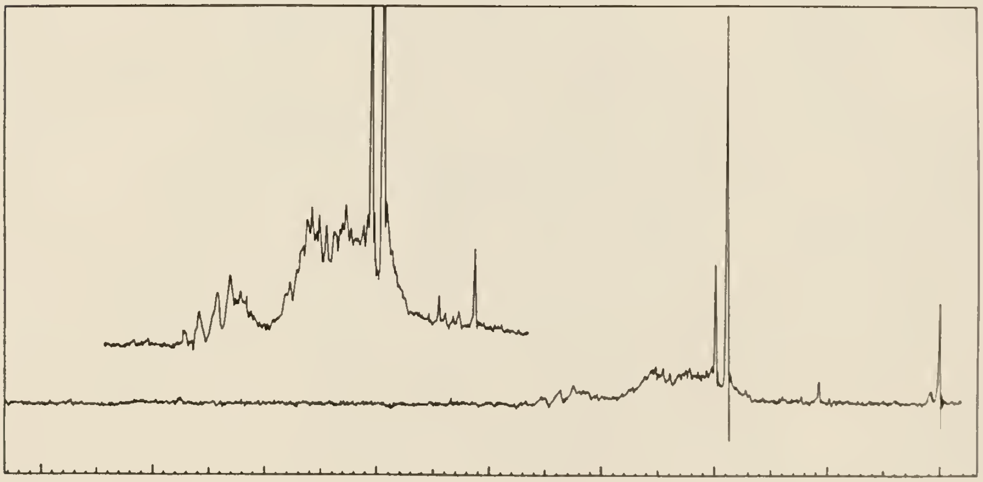

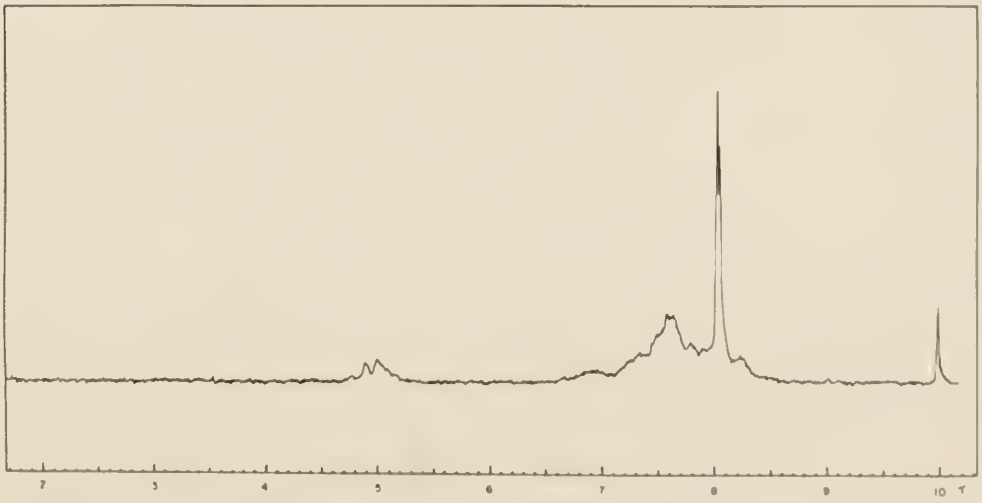
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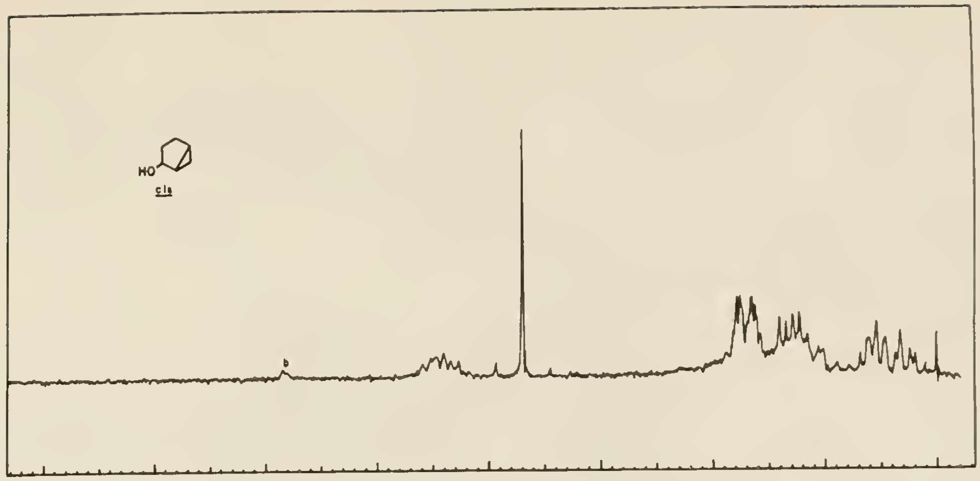
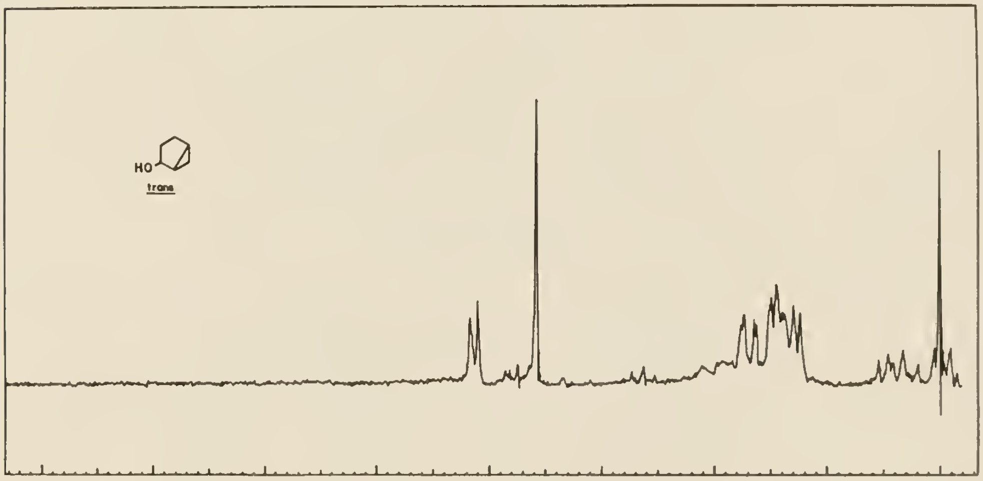
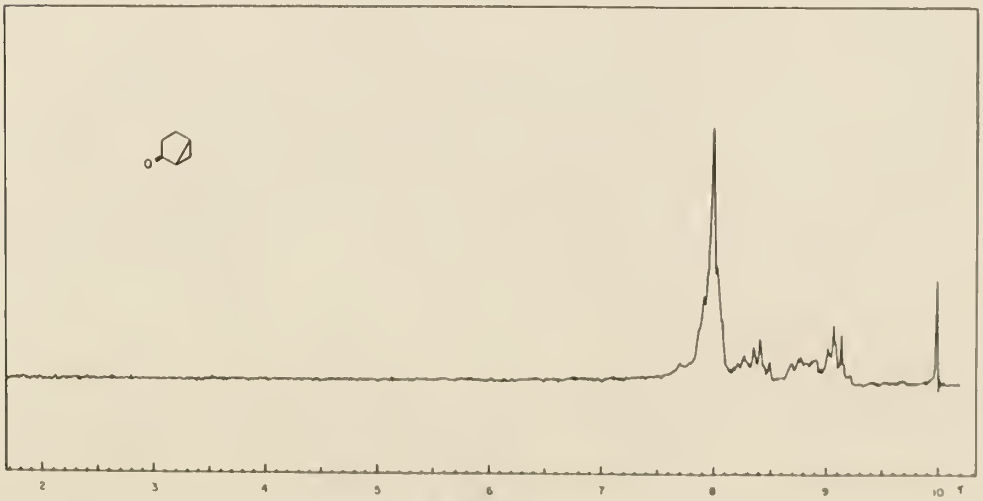

HO
cis
b


HO
trans


O
2
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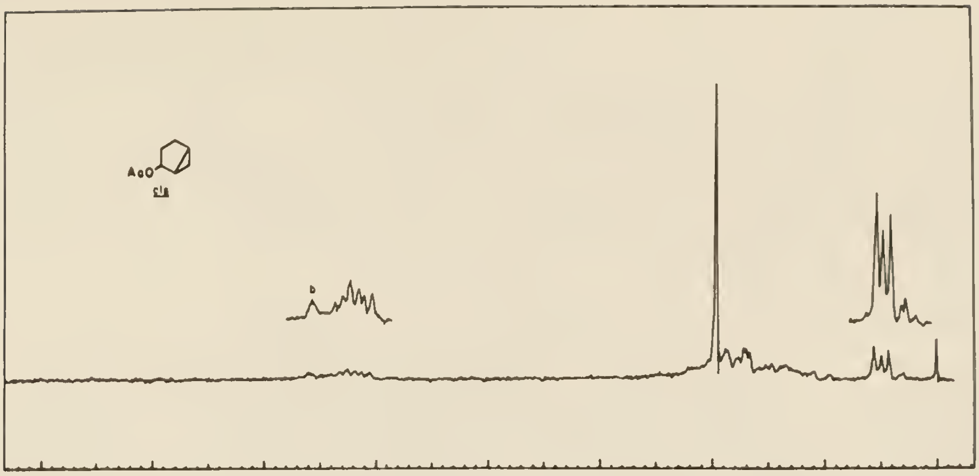
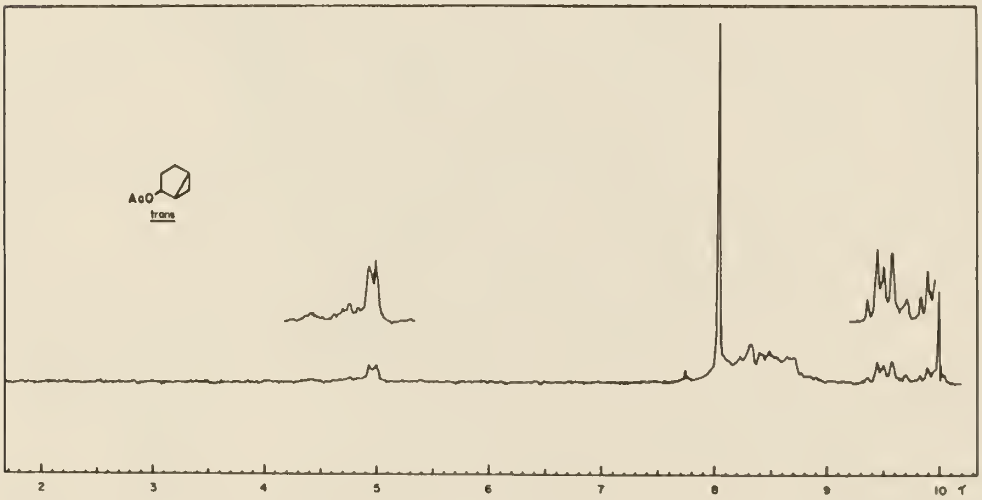

AcO
cis
b


AcO
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EXPERIMENTAL[119]

Dimethyl Acetylenedicarboxylate. The procedure of Huntress, Lesslie, and Bornstein[48] was followed to give a yield of 75%, b.p. 94-96°/20 mm. (lit.[48] 72-88% yield, b.p. 95-98°/19 mm.). The infrared spectrum was in agreement with that published[76]. The n.m.r. spectrum showed a singlet absorption at τ 6.05.

cis-3,4-Dichlorocyclobutene. The procedure followed was that of Avram, Dinulescu, Elian, Farcasiu, Marica, Maeescu, and Nenitzescu[1].

1. Chlorination of Cyclooctatetraene with Sulfuryl Chloride. A longer and varied induction period was observed due to the inhibitor present in the cyclooctatetraene[117]. In a single attempt with pure cyclooctatetraene (Aldrich Chemical Co.), an induction period of 20 minutes was observed (lit.[1] 15 minutes). Sodium bicarbonate rather than calcium carbonate was used to neutralize the reaction mixture. After drying, this product was used directly in the next step.

2. Reaction with Dimethyl Acetylenedicarboxylate. The reaction mixture was allowed to reflux four hours instead of the suggested three.

3. Pyrolysis. Three volatile fractions were obtained. The first fraction, a yellow liquid with b.p. 35°/90 mm., distilled at bath temperatures 105-173°. The second fraction, a clear, colorless liquid with b.p. 119-137°/65 mm., distilled at bath temperatures 173-195° (lit.[1] b.p. 110-140°/65 mm. at a bath temperature of 180°). The last fraction, a clear, light yellow liquid with b.p. 93°/1 mm., distilled at a bath temperature of 125°. The second portion was purified by fractional distillation on a 30 cm. semimicro spinning band column. The first fraction to come off was near pure trans,trans-1,4-dichlorobutadiene, b.p. 60°/60 mm. (lit.[1] b.p. 60°/68 mm.). The infrared (page 45) and n.m.r. (page 57) spectra were

recorded. The second fraction was pure *cis*-3,4-dichlorocyclobutene, b.p. 74°/58 mm., $n_D^{25.5}$ 1.4983 (lit.[1] b.p. 74°/60 mm., n_D^{25} 1.49832). The infrared (page 45) and n.m.r. (page 57) spectra were recorded. The two products (76% yield) were analyzed by vapor phase chromatography (g.c.) on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at 175°. The flow rate was 60 ml./minute, the detector temperature was 290°, and the injection port temperature was 250°. The *trans*,*trans*-1,4-dichlorobutadiene had a retention time of 3.1 minutes and the *cis*-3,4-dichlorocyclobutene had a retention time of 6.1 minutes.

Dichloroacetyl Chloride. Dichloroacetic acid (109.6 g., 0.85 mole), thionyl chloride (165.4 g., 1.40 mole), and a catalytic amount of dimethyl formamide were combined and heated at reflux for 6 hours. The reaction mixture was distilled through a 30 cm. Vigreux column to give a light yellow liquid, (59.25 g., 52% yield) b.p. 104° (lit.[110] 107-108°). The infrared spectrum was in agreement with that published[75].

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one. This bicyclic ketone was prepared by the procedure of Stevens, Reich, Brandt, Fountain, and Gaughan[100] in 65% yield, b.p. 33°/0.2 mm. (lit.[100] 70-75% yield, b.p. 38°/0.25 mm.). The product was shown to be 96% pure by g.c. analysis using a 6 x ¼" Carbowax 20M column (20% on Chromosorb W) at 175°. The flow rate was 60 ml./minute, the detector temperature was 305°, and the injection port temperature was 300°. The ketone had a retention time of 12.0 minutes. The infrared and n.m.r. spectra agreed with those reported[100].

Reaction of cis-3,4-Dichlorocyclobutene with Dichloroketene. The procedure for this reaction was patterned after that of Stevens, Reich, Brandt, Fountain, and Gaughan[100]. Triethylamine (0.95 g., 9.0 mmole) in 24 ml. of hexane was added over a period of 5 hours to a solution of *cis*-3,4-dichlorocyclobutene (3.0 g., 24.0 mmole) and dichloroacetyl chloride (1.25 g., 8.5 mmole) in 5 ml. of hexane. The reaction mixture was maintained at -1 to +1°. The solid hydrochloride was filtered from the reaction mixture, and trap-to-trap distillation through a short path column (27°/0.1 mm.) yielded a clear, colorless liquid (2.48 g.) and a non-volatile dark brown viscous oil. Analysis of these two components by g.c. using a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at 175° showed a major peak at 2.1 minutes for cis-3,4-dichlorocyclobutene and a trace component at 4.1 minutes that could not be identified. The pot residue showed only residual starting material. The gas flow was 60 ml./minute, the detector temperature was 304°, and the injection port temperature was 305°. An infrared spectrum of the distillate agreed with that of the starting cyclobutene.

Diiron Enneacarbonyl. This compound was prepared by a modification of the method of Speyer and Wolf[94]. Iron pentacarbonyl (200 g., 1.02 mole) in 410 ml. of glacial acetic acid was maintained under a nitrogen atmosphere while being irradiated with a GE-AH4 ultraviolet lamp (with the Pyrex envelope removed) in a quartz, water cooled well. At the end of 37 hours the solid product was filtered from the reaction mixture, washed repeatedly with anhydrous ether and air dried (100.9 g.). The mother liquor (without ether) was irradiated for another 70.6 hours and the golden crystals were worked-up as before (42.7 g.). The total yield was 143.6 g. (81%) with a total reaction time of 107.6 hours. Dry diiron enneacarbonyl is stable toward oxygen and moisture, but burns spontaneously in the air if moistened with iron pentacarbonyl.

Reaction of cis-3,4-Dichlorocyclobutene with Diiron Heptacarbonyl Tetraiodide. Diiron enneacarbonyl (6.0 g., 16.0 mmole) was added to a solution of iodine (4.1 g., 16.0 mmole) in 50 ml. of pentane. A gas was immediately evolved and the temperature of the solution rose approximately 3°. After the initial reaction had subsided, *cis*-3,4-dichlorocyclobutene (2.0 g., 16.0 mmole) was added, and the mixture refluxed for 24 hours. The reaction mixture was cooled, filtered from the solid residue, washed with aqueous sodium thiosulfate, and dried over magnesium sulfate. The product was concentrated by distillation of the solvent through a 30 cm. Vigreux column. The pot residue was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at 165°. The flow rate was 60 ml./minute, the detector temperature was 302°, and the injection port temperature was 285°. Six peaks were observed with the ones at 6.4, 7.9, and 8.4 minutes being too small for collection. The major peaks at 22.0, 26.1, and 29.2 minutes were collected and their infrared spectra recorded. The infrared spectrum of the first liquid product (peak at 22.0 minutes) corresponded to that published by Avram, Dinulescu, Marica, Mateescu, Sliam, and Nenitzescu[2] for *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene. The infrared spectrum of the peak at 26.1 minutes corresponded to that published for *anti*-tricyclo[4.2.0.0^{2,5}]-octa-3,7-diene[2]. The two isomers were present in a ratio of 2:3. Both of these two isomers polymerized on standing at room temperature for 36 hours. The third product was a white crystaline solid that could not be identified. This material showed infrared absorptions (solid in nujol) at 3.46(s), 3.56(sh), 6.5(w), 6.85(s), 7.28(m), 7.8(w), 8.72(m), 10.36(s), and 13.83(w) μ. The infrared spectrum of the crude product mixture showed absorptions at 7.69(w), 7.85(s), 8.09(w), 8.56(s), 8.66(s), 8.88(sh), 9.03(s), 9.95(w), 10.37(w), 11.0(w), 11.57(s), 12.85(sh), 13.35(s), and 14.25(m) μ. Collection of the entire sample from the g.c. gave a mixture of compounds which showed infrared absorptions at 3.3(m), 5.74(w), 5.93(w), 6.27(m), 6.5(s), 7.72(s), 7.85(sh), 7.88(s), 8.27(m), 8.75(s), 9.6(w), 10.43(m), 10.55(s), 11.05(w), 12.7(m), 13.9(sh), and 14.16(m) μ. The product mixture could not be separated by either liquid chromatography on alumina, or thin-layer chromatography on silica gel.

Cyclobutadieneiron Tricarbonyl. A modification of the procedure of Emerson, Watts, and Pettit[36] was used to prepare this compound. *cis*-3,4-Dichlorocyclobutene (4.0 g., 32.4 mmole), diiron enneacarbonyl (16.5 g., 45.4 mmole), and 140 ml. of pentane were heated under reflux with a nitrogen atmosphere at a bath temperature of 47-48° for 5.25 hours. The reaction mixture was cooled to room temperature and the deep green liquid filtered, under a nitrogen atmosphere, from the solid residue. The solvent and iron pentacarbonyl were removed from the complex by distillation through a short path column at reduced pressure. The product distilled as a bright yellow liquid (3.02 g., 48%, lit.[36] 40%) at 27°/0.5 mm. and solidified to a bright yellow solid when cooled below room temperature. The distillate was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 175°. The gas flow was 60 ml./minute, the detector temperature was 307°, and the injection port temperature was 303°. Two major peaks were observed at 0.45 and 3.45 minutes. The peak at 3.45 minutes was collected in a Dry Ice-isopropyl alcohol bath as a clear, colorless liquid which evaporated as the material was allowed to warm toward room temperature. No starting cyclobutene, and only a trace of diiron enneacarbonyl could be observed. The n.m.r. spectrum showed a singlet absorption at τ 6.09 (lit.[36] τ 6.09). The infrared spectrum (page 45) was recorded. Cyclobutadieneiron tricarbonyl slowly decomposes in the presence of air or moisture to give a reddish-brown solid not soluble in water or organic solvents.

Dimethyl Bicyclo[2.2.0]hexa-2,5-diene-2,3-dicarboxylate. A procedure patterned after that of Watts, Fitzpatrick, and Pettit[107] was used to prepare this compound. Ceric ammonium nitrate (9.5 g., 17.0 mmole) in 17 ml. of distilled water was added to a mixture of cyclobutadieneiron tricarbonyl (1.0 g., 5.2 mmole), and dimethyl acetylenedicarboxylate (7.39 g., 52.0 mmole) in 38 ml. of 95% ethyl alcohol. The addition time was 30 minutes and the reaction temperature was maintained between -2 and +2°. Bubbles were noted coming from the reaction mixture as the ceric ion solution was rapidly decolorized upon addition. The reaction mixture was stirred for an additional 15 minutes at -1°, extracted with six 20 ml. portions of pentane, six 20 ml. portions of ether, and the two extracts washed separately with three 20 ml. portions of water. The dried organic extracts were chromatographed on silica gel. Dimethyl acetylenedicarboxylate was eluted with methylene chloride, and a 1:3 solution of ether and methylene chloride eluted a mixture of the desired "Dewar benzene" and its aromatic isomer (0.69 g., 68% yield). G.c. analysis of this fraction on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) showed two major peaks. The column temperature was 175° until it was raised to 225° at the end of 9 minutes. The flow rate was 60 ml./minute, the detector temperature was 305°, and the injection port temperature was 296°. The first peak (15.3 minutes) was identified as an impurity in the dimethyl acetylenedicarboxylate. The second peak (23.0 minutes), when compared by infrared spectra to an authentic sample, was shown to be pure dimethyl phthalate. The n.m.r. spectrum (page 57) of the chromatographed product mixture was consistent with that published[107,118], and the infrared spectrum (page 47) was recorded.

Ceric Ion Oxidation of Selected Dienophiles. The dienophile was added to a water-alcohol solution of ceric ammonium nitrate, stirred, and allowed to stand at room temperature. The following observations were made.

1. 2-Butenone. Upon the addition of the ketone, the beginning blood red color of the ceric ion solution immediately changed to yellow. Noticeable heating of the reaction mixture occurred and in a few minutes a red polymer had formed.

2. Methyl Acrylate. The color of the solution was unchanged for approximately 10 minutes. After 30 minutes a yellow solution remained and some polymer had formed.

3. Vinyl Acetate. No color change was noted for the first 0.5 hour, but at the end of 1.5 hours the solution was nearly colorless. After 3 hours the solution turned red again, and while standing overnight a red polymer formed.

4. 2-Butynone. No immediate color change was noted, but after 45 minutes the solution had turned a light yellow, and a polymer formed while standing overnight.

Reaction of Cyclobutadieneiron Tricarbonyl, Vinyl Acetate, and Ceric Ion. This reaction was patterned after the procedure of Watts, Fitzpatrick, and Pettit[108]. Cyclobutadieneiron tricarbonyl (0.6 g., 3.1 mmole) in 1.5 ml. of 95% ethyl alcohol was slowly added over a 10 minute period to a mixture of ceric ammonium nitrate (9.5 g., 17.0 mmole), vinyl acetate (4.5 g., 52 mmole), 36.5 ml. of 95% ethyl alcohol, and 17 ml. of water. The reaction mixture was maintained between -2 and +1°. During the addition bubbles were given off and the initial blood red color of the ceric ion solution lessened somewhat in intensity. The reaction mixture was stirred an additional 15 minutes, extracted with six 20 ml. portions of pentane and dried over magnesium sulfate. The solvent was distilled from the dry solution through a 30 cm. Vigreux column, and the remaining yellow oil (0.15 g.) was distilled through a short path column (27°/0.05 mm.) yielding only a trace of volatile material. This product mixture was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 125°. The flow rate was 60 ml./minute, the detector temperature was 279°, and the injection port temperature was 203°. Peaks were observed at 0.9, 1.1, 1.25, 1.4, 1.8, 2.0, 2.2, 2.65, 3.5, 4.1, 5.0, 5.95, 7.4, 8.3, and 14.4 minutes. No identifiable compounds could be obtained from this mixture.

In another attempt, an aqueous solution of ceric ammonium nitrate was added to the reaction mixture instead of cyclobutadieneiron tricarbonyl. The results of this attempt were the same as those above.

Methyl endo-Bicyclo[2.2.0]hex-5-ene-2-carboxylate. This reaction was patterned after the procedure of Watts, Fitzpatrick, and Pettit[108]. Ceric ammonium nitrate (10.0 g., 18.2 mmole) in 22 ml. of water was added over a 15 minute period to a solution of cyclobutadieneiron tricarbonyl (1.0 g., 5.2 mmole), and methyl acrylate (4.49 g., 52 mmole) in 40 ml. of 95% ethyl alcohol. The reaction mixture was maintained at 0 to -2°. Bubbles were given off during the addition of the ceric ion solution. The reaction mixture was extracted with six 20 ml. portions of ether, the ether extract washed with several portions of water, and the resulting solution dried over magnesium sulfate. The concentrated reaction mixture was chromatographed on silica gel. The fraction eluted with 1:1 ether-methylene chloride was distilled through a short path column (27°/0.05 mm.) to yield a clear, colorless liquid (0.02 g., 3%). This material was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 175°. The flow rate was 60 ml./minute, the detector temperature was 304°, and the injection port temperature was 293°. Two major peaks were observed at 1.8 and 4.8 minutes. An n.m.r. spectrum of this fraction showed absorptions as a multiplet centered at τ 3.58, a singlet at τ 6.25, and continuous absorption from τ 6.0-8.17. The infrared spectrum was not recorded.

Catalytic Hydrogenation of Methyl endo-Bicyclo[2.2.0]hex-5-ene-2-carboxylate. Methyl endo-bicyclo[2.2.0]hex-5-ene-2-carboxylate (50 mg.) in methylene chloride-ethanol solution was hydrogenated for 5 hours over platinum in a semimicro hydrogenation apparatus. No hydrogen uptake could be measured due to the amount of material involved. At the end of the reaction period the product mixture was filtered and concentrated leaving a light yellow liquid (25 mg., 50%). This mixture was analyzed by g.c. under the conditions listed above. A single peak was observed at 1.7 minutes. The column temperature was raised to 225° at 9.0 minutes and two more peaks were observed at 10.8 and 12.7 minutes. No conclusive n.m.r. or infrared spectra could be obtained.

2-Butynone.

1. Ethynylmagnesium Bromide. The procedure of Skattebol, Jones, and Whiting[92] was followed to prepare this compound. Ethyl bromide (120 g., 1.1 mole) and magnesium turnings (24 g., 1.0 mole) were combined in 400 ml. of tetrahydrofuran to produce the initial ethylmagnesium bromide. This compound was used immediately in the next step.

2. Reaction of Ethynylmagnesium Bromide with Acetic Anhydride. The procedure followed was that used by Kroeger and Nieuwland[52] to prepare substituted acetylenic ketones. The compound prepared above was added over 1.25 hours to 204 g. (2.0 mole) of acetic anhydride in 200 ml. of ether. The reaction temperature was -25° and a nitrogen atmosphere was maintained over the solution. After the addition, the mixture was stirred an additional 6 hours, hydrolyzed with 50 ml. of water, filtered from the resulting polymer, washed with five 1000 ml. portions of water, dried, and distilled from a 36 inch spinning band column. The clear, colorless liquid (6.15 g.,

9% yield) had a boiling point of 35°/130 mm. (lit.[9] 84.5-86°) and exhibited one major peak at 2.04 minutes when analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 75°. The flow rate was 60 ml./minute, the detector temperature was 305°, and the injection port temperature was 313°. The infrared spectrum of the purified compound showed absorptions at 3.12(s), 3.41(w), 4.79(s), 5.76(sh), 5.92(s), 7.03(m) 7.35(m), 8.01(m), 8.32(s), 9.54(w), 9.76(m), 10.17(s), and 13.46(s) μ. The n.m.r. spectrum showed singlet absorptions at τ 6.45 and 7.65.

Bicyclo[2.2.0]hexa-2,5-dien-2-yl Methyl Ketone. A procedure patterned after that used for the preparation of dimethyl bicyclo[2.2.0]hexa-2,5-diene-2,3-dicarboxylate (described above) was employed for the preparation of this compound. Ceric ammonium nitrate (10.0 g., 18.2 mmole) in 22 ml. of distilled water was added to a mixture of cyclobutadieneiron tricarbonyl (1.0 g., 5.2 mmole) and 2-butynone (1.77 g., 26.0 mmole) in 40 ml. of 95% ethanol. The reaction was maintained at -1 to -3° during an addition time of 70 minutes. After the addition the solution was stirred for another 30 minutes and 0.2 g. of ferrous ammonium sulfate added. This mixture was stirred an additional 10 minutes, extracted with five 40 ml. portions of ether, and the ether washed with five 40 ml. portions of water. The resulting ether extract was dried, concentrated at reduced pressure and distilled through a short path column (27°/0.05 mm.) to yield 0.17 g. (27%) of a light yellow liquid. G.c. analysis of this product on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 175° showed only one major peak at 2.25 minutes. The flow rate was 60 ml./minute, the detector temperature was 304°, and the injection port temperature was 317°. This peak when collected and compared to an authentic sample was shown to be pure acetophenone. The infrared (page 47) and n.m.r.[118] (page 59) spectra were recorded.

Potassium Azodicarboxylate. This compound was prepared according to the method of Thiele[101]. Azodicarbonamide (0.42 g., 5.0 mmole) and 1 ml. of aqueous potassium hydroxide (1:1) were combined at 0° and stirred until the evolution of ammonia stopped. The bright yellow precipitate which formed was filtered and washed repeatedly with absolute alcohol. The resulting crystaline solid was used directly in the next step.

Reaction of Diimide with Bicyclo[2.2.0]hexa-2,5-dien-2-yl Methyl Ketone. The method of van Tamelen, Dewey, and Timmons[102] was used in this reaction. Glacial acetic acid (0.63 ml., 10 mmole) in 5 ml. of absolute ethanol was added, under nitrogen, to a mixture of potassium azodicarboxylate and bicyclo[2.2.0]hexa-2,5-dien-2-yl methyl ketone (0.15 g., 1.2 mmole) in 10 ml. of absolute ethanol. The addition was complete after 1 hour and the resulting mixture was stirred for an additional 6 hours, added to 75 ml. of ether, washed with four 30 ml. portions of water, dried, concentrated at reduced pressure, and distilled through a short path column (27°/0.05 mm.). The distillate product mixture (0.03 g., 20%) was shown to contain thirteen components by g.c. analysis on a 6' x ½" Carbowax 20M column (20% on Chromosorb W). The column temperature was programmed from 135° to 160° at a rate of 3.2°/minute, the flow rate was 60 ml./minute, the detector temperature was 255°, and the injection port temperature was 229°. The three major peaks appeared at 2.15 (20.0%), 3.7 (37.8%), and 6.9 (12.1%) minutes. The collected peak at 3.7 minutes was identified as acetophenone by infrared spectral and g.c. retention time comparisons with an authentic sample. No other collected peaks were large enough for spectral data.

Methyl Propiolate.

1. Propiolic Acid. The method of Perkin and Simonsen[68] was used to

prepare this compound in a 99% yield. The acidified reaction mixture was saturated with sodium chloride rather than ammonium sulfate and the ether solution was dried over magnesium sulfate rather than calcium chloride. This compound was used immediately in the next reaction without further purification.

2. Esterification of Propiolic Acid. The method of James and Fanta[49] was followed to prepare the desired ester in a yield of 37%, b.p. 101° (lit.[49] 49% yield, 96-102.5°). G.c. analysis of the product on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 100° showed one major peak at 1.35 minutes. The flow rate was 60 ml./minute, the detector and injection port temperatures were 304°. The compound showed infrared absorptions at 3.12(s), 3.44(w), 4.73(s), 5.83(s), 6.98(s), 7.99(s), 8.39(m), 8.86(w), 10.06(m), 11.57(s), and 13.15(s) μ. The n.m.r. spectrum showed singlet absorptions at τ 6.24 and 7.02.

Methyl Bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate. This compound was prepared by a procedure patterned after that of Watts, Fitzpatrick, and Pettit[107]. Ceric ammonium nitrate (50.0 g., 91 mmole) in 110 ml. of distilled water was added to a mixture of cyclobutadieneiron tricarbonyl (5.4 g., 28.1 mmole) and methyl propiolate (21.9 g., 0.26 mole) in 200 ml. of 95% ethanol. The reaction was maintained at -1 to -3° during an addition time of 1.5 hours. After the addition, the solution was stirred for another 15 minutes and 0.2 g. of ferrous ammonium sulfate added. This mixture was stirred an additional 10 minutes, extracted with five 40 ml. portions of ether, and the ether washed with five 40 ml. portions of water. The resulting ether extract was dried, concentrated at reduced pressure, and distilled through a short path column (27°/0.05 mm.) to yield 1.88 g. (49%) of a light yellow liquid. G.c. analysis of this product on a 6' x ¼"

Carbowax 20M column (20% on Chromosorb W) at a temperature of 125° showed 4 major peaks at 1.0, 1.4, 1.7, and 5.5 minutes. The flow rate was 60 ml./minute, the detector temperature was 304°, and the injection port temperature was 306°. The collected peak at 5.5 minutes, when compared by infrared spectral and g.c. retention times to an authentic sample, was shown to be pure methyl benzoate. The desired "Dewar benzene" and its aromatic isomer were shown by g.c. integration to be 63% of the product mixture. The n.m.r. spectrum (page 59) agreed with that published[107], and integration of the spectrum indicated that the desired diene was 39% of the "Dewar benzene", aromatic isomer mixture. The infrared spectrum (page 47) was recorded.

Catalytic Hydrogenation of Methyl Bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate. Methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (0.2 g.) in 10 ml. of absolute alcohol was hydrogenated for 5.5 hours over platinum in a semi-micro hydrogenation apparatus. No hydrogen uptake was observed. At the end of the reaction period the product mixture was filtered and concentrated at reduced pressure. The infrared spectrum agreed exactly with that of methyl benzoate. No peaks attributed to the "Dewar benzene" were present. G.c. analysis under the conditions listed above showed that the aromatic peak at 5.5 minutes had not changed its relative concentration.

Methyl endo-Bicyclo[2.2.0]hexane-2-carboxylate. The method of van Tamelen, Dewey, and Timmons[102] was used to prepare this compound. Glacial acetic acid (12.65 ml., 13.26 g., 0.222 mole) in 30 ml. of methanol was added, under nitrogen, to a mixture of potassium azodicarboxylate (prepared, as described earlier, from 9.32 g. (0.111 mole) of azodicarbonamide) and methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (1.2 g., 8.8 mmole) in 200 ml. of methanol and 50 ml. of water. The addition was complete after 3.5 hours, the resulting mixture was stirred for an additional 4 hours, and added to 500 ml. of ether. The resulting ether solution was washed with eight 100 ml. portions of water, dried, concentrated under reduced pressure, and distilled through a short path column (27°/0.05 mm.). The distillation product mixture was shown to contain three major components at 4.4, 7.6, and 11.3 minutes by g.c. analysis on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 125°, and raised to 225° at the end of 9 minutes. The flow rate was 60 ml./minute, the detector temperature was 252°, and the injection port temperature was 223°. The first peak (4.4 minutes) contained no carbonyl, and the collected peak at 11.3 minutes was identified as methyl benzoate by infrared spectral and g.c. retention time comparisons with an authentic sample. The peak at 7.6 minutes (0.44 g., 36.7%) was collected and the infrared (page 49) and n.m.r. (page 61) spectra recorded. If the 39% figure for the amount of "Dewar benzene" present in the starting reaction mixture is correct, then this reduction proceeded in 93% to the corresponding saturated system.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.55; H, 8.63.
Found: C, 68.67; H, 8.82.

In a single run using ethanol instead of methanol, the corresponding ethyl esters were isolated. The mass spectrum (page 29) of the ethyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate showed a parent ion at m/e 154 and the 100% peak at m/e 81 corresponding to $C_6H_9^+$.

Attempted Base Equilibration of Methyl endo-Bicyclo[2.2.0]hexane-2-carboxylate. Methyl *endo*-bicyclo[2.2.0]hexane-2-carboxylate (50 mg.), sodium metal (5 mg.), and 0.3 ml. of anhydrous methanol were stirred together for 48 hours at room temperature. At the end of this period the reaction mixture was added to 5 ml. of water, extracted with four 10 ml. portions of ether, dried over magnesium sulfate, concentrated at reduced pressure, and distilled through a short path column (27°/0.05 mm.) to yield 10 mg. of a clear, colorless liquid. An n.m.r. spectrum identified this as the starting endo-ester. The aqueous portion of the reaction work-up was acidified with dilute hydrochloric acid, extracted with ether, dried, and esterified with diazomethane. An n.m.r. spectrum of the resulting ester (30 mg.) identified it as the starting endo isomer.

Acid Equilibration of Methyl endo-Bicyclo[2.2.0]hexane-2-carboxylate. Methyl endo-bicyclo[2.2.0]hexane-2-carboxylate (30 mg.), 6 ml. of anhydrous methanol, and 4 drops of concentrated sulfuric acid were stirred together for 13 days at room temperature. At the end of this period the reaction mixture was diluted with 20 ml. of ether, washed with three 10 ml. portions of water, dried, concentrated at reduced pressure, and distilled through a short path column (27°/0.05 mm.). The clear, colorless distillate was analyzed by g.c. and found to have the same retention time as the starting endo-ester. A mixture of the distillation product and the starting ester gave a single peak under the conditions listed above. The infrared (page 49) and n.m.r. (page 61) spectra were recorded. The purity of the methyl exo-bicyclo[2.2.0]hexane-2-carboxylate is unknown, but can be assumed to be good due to the length of the reaction.

Ethyl Cyclohexanecarboxylate. Cyclohexanecarboxylic acid (25 g., 0.195 mole), was combined with 38 ml. of absolute ethanol and 3 ml. of concentrated sulfuric acid, and refluxed for 15 hours. At the end of this period the reaction mixture was added to 100 ml. of ether, washed with water, saturated sodium bicarbonate solution, and water. The resulting ether solution was dried and distilled through a 30 cm. Vigreux column to give the product in 75% yield (22.7 g.), b.p. 58°/4.5 mm., n_D^{27} 1.4380 (lit.[112] b.p. 196°,

n_D^{25} 1.4396). The infrared spectrum was in agreement with that published[79].

Formation of Acetylcyclohexane from Ethyl Cyclohexanecarboxylate. This compound was prepared by the method of Corey and Chaykovsky[22].

1. Methylsulfinylmethyl Cyclohexyl Ketone. This compound was prepared as described to give 95% crude yield, 67% purified yield. The impurity was found by infrared spectral comparisons to be cyclohexanecarboxylic acid.

2. Reduction with Aluminum Amalgam. This reaction was carried out as described except that a 90% aqueous tetrahydrofuran solution was used instead of the 10% one listed. The desired methyl ketone was obtained in 95% yield (lit.[22] 98.5%), $n_D^{26.5}$ 1.4474 (lit.[111] $n_D^{25.9}$ 1.4496). The infrared spectrum showed absorptions at 3.46(s), 3.55(m), 5.85(s), 6.90(m), 7.02(sh), 7.30(m), 7.40(m), 7.65(w), 7.75(w) 8.05(w), 8.46(w), 8.55(m), 9.63(w), 10.35(w), 11.23(w), and 12.63(w) μ.

Cyclohexyl Acetate. This compound was prepared in two ways following a procedure patterned after that of Wiberg and Hess[114].

1. Formation with m-Chloroperbenzoic Acid. Acetylcyclohexane (0.75 g., 5.6 mmole) and 80% m-chloroperbenzoic acid (1.47 g., 8.6 mmole) were combined in 11 ml. of methylene chloride and stirred at room temperature for 10 days. The progress of the reaction was followed by titrating the unreacted peracid[90]. The reaction was 83% complete after 2 days and 95% complete after ten. The reaction mixture was washed with three 3 ml. portions of cold 10% sodium hydroxide, 8 ml. of water in two portions, 2.5 ml. of 10% sodium bisulfite, and 2.5 ml. of water. The resulting solution was dried, concentrated, and distilled through a short path column (27°/0.05 mm.) to yield 0.63 g., 75%, $n_D^{29.5}$ 1.4362 (lit.[109] n_D^{20} 1.4401). The distillate was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W)

at 125°. The flow rate was 60 ml./minute, the detector temperature was 304°, and the injection port temperature was 303°. One major peak was observed at 1.7 minutes and no starting ketone could be observed. The infrared spectrum of the collected sample was in agreement with that published[78].

2. Formation with Peracetic Acid. This reaction was run as described above using 47% peracetic acid. The reaction was 45% complete after 2 days and 83% complete after ten. The product mixture (75% yield) was analyzed by g.c. as described above. Two major peaks were observed at 1.7 (86%) and 2.3 (14%) minutes. The second peak corresponded by infrared spectral and g.c. retention time comparisons to that of the starting ketone.

Cyclohexanecarbonyl Chloride. This compound was prepared by a procedure patterned after that of Wiberg, Lowry, and Colby[113]. A mixture of cyclohexanecarboxylic acid (5.0 g., 39.0 mmole), thionyl chloride (10.0 g., 78.0 mmole), and 5 drops of dimethylformamide was combined under a nitrogen atmosphere and stirred at room temperature for 1 hour, and then heated at reflux for 4 hours. The excess thionyl chloride was removed at reduced pressure and the product distilled through a short path column (27°/0.05 mm.) to yield 5.29 g., 93%. The infrared spectrum agreed with that published[77].

Dimethyl Cadmium. Methylmagnesium bromide was prepared by the method of Colonge and Marey[20]. This compound was used immediately in the formation of dimethyl cadmium prepared by the method of Cason[16]. The resulting product was used immediately in the next reaction.

Formation of Acetylcyclohexane from Cyclohexanecarbonyl Chloride. This compound was prepared by a procedure patterned after that of Wiberg, Lowry, and Colby[113]. Cyclohexanecarbonyl chloride (0.5 g., 3.4 mmole) in 1 ml. of benzene was added under nitrogen to 15 ml. (5.0 mmole) of dimethyl cadmium-benzene solution (prepared above) over a 10 minute period. The reaction mixture was stirred at room temperature for 2 hours, and a saturated solution of ammonium chloride slowly added. The layers were separated and the aqueous layer was extracted with ether. The combined organic layer and ether extract was washed twice with water and dried over magnesium sulfate. The dried solution was concentrated at reduced pressure and distilled through a short path column (27°/0.05 mm.) to yield 0.39 g., 91%. The infrared spectrum agreed with that for the compound obtained by the previously described method.

endo-Bicyclo[2.2.0]hex-2-yl Methylsulfinylmethyl Ketone. The general procedure of Corey and Chaykovsky[22] was followed to prepare this compound.

1. *Methylsulfinyl Carbanion*. Sodium hydride (0.556 g., 10 mmole, 44%) was allowed to react with 1.3 ml. of dimethyl sulfoxide as described.

2. *Reaction of Methylsulfinyl Carbanion with Methyl endo-Bicyclo[2.2.0]hexane-2-carboxylate*. A solution of tetrahydrofuran (1.3 ml.) and methylsulfinyl carbanion (prepared above) was cooled in an ice bath during the addition of the ester (under nitrogen) over a 10 minute period. The reaction mixture was stirred 1 hour at room temperature, 7.8 ml. of water added, the resulting solution acidified with dilute hydrochloric acid to pH 3, and the resulting mixture extracted with three 40 ml. portions of chloroform. This extract was washed with three 20 ml. portions of water, dried, and concentrated at reduced pressure to yield 0.86 g. (>95% yield) of a yellow oil. Trituration with cold iospropyl ether and ethyl ether gave 0.28 g. of a white solid and 0.58 g. of a yellow oil. The solid was identified by its n.m.r. spectrum as ω-(methylsulfinyl)acetophenone produced from the methyl benzoate impurity. The infrared (page 51) and n.m.r.

(page 61) spectra of the desired yellow oil were recorded. This product was used directly in the next reaction.

Reduction of endo-Bicyclo[2.2.0]hex-2-yl Methylsulfinylmethyl Ketone. A procedure patterned after that of Corey and Chaykovsky[22] was used for this reaction.

1. Aluminum Amalgam. Aluminum foil (0.83 g., 31.0 mmole) was rinsed with absolute alcohol and anhydrous ether, immersed in concentrated mercuric chloride solution for 45 seconds, rinsed with absolute alcohol and anhydrous ether, and used immediately in the following reaction.

2. Formation of Bicyclo[2.2.0]hex-2-yl Methyl Ketone. The aluminum amalgam prepared above was added, in small pieces, to *endo*-bicyclo[2.2.0]-hex-2-yl methylsulfinylmethyl ketone (0.58 g., 3.0 mmole) in 36 ml. of 90% aqueous tetrahydrofuran. The reaction mixture was stirred at reflux for 2 hours, cooled, filtered from the solid residue, and concentrated by distillation of the solvent through a 30 cm. Vigreux column. The concentrated product mixture was added to 250 ml. of ether, dried over magnesium sulfate, concentrated, and distilled through a short path column (27°/0.05 mm.) to yield 0.20 g. (85%) of a clear, colorless liquid. This mixture was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 125°. The flow rate was 60 ml./minute, the detector temperature was 252°, and the injection port temperature was 224°. One major peak was observed at 2.55 minutes. The infrared (page 51) and n.m.r. (page 63) spectra of this material collected from the g.c. was recorded. Integration of the n.m.r. spectrum gave a ratio of 62:38, *exo*- to *endo*-bicyclo[2.2.0]-hex-2-yl methyl ketone.

exo-Bicyclo[2.2.0]hex-2-yl Acetate. This compound was prepared by the procedure used above for the formation of cyclohexyl acetate. The mixture of *exo*- and *endo*-bicyclo[2.2.0]hex-2-yl methyl ketone (0.19 g., 1.5 mmole) prepared above, was added to 0.37 g. (2.1 mmole) of 80% *m*-chloroperbenzoic acid in 2.8 ml. of methylene chloride. The reaction mixture, after stirring at room temperature for 3 days, yielded 0.19 g. (89%) of a clear, colorless liquid. This liquid was analyzed by g.c. on a 7½' x ¼" Carbowax 20M column (20% on Chromosorb W) at a starting temperature of 125° and changed to 135° at 5.5 minutes. Two major peaks were observed at 7.0 and 7.85 minutes. The collected peak at 7.0 minutes (91% of the product mixture) was identified as pure *exo*-bicyclo[2.2.0]hex-2-yl acetate by comparison with the published n.m.r. spectrum of McDonald and Reineke[61]. The peak at 7.85 minutes was identified as a mixture of *cis*-bicyclo[3.1.0]hex-2-yl acetate (9%), 3-cyclohexenyl acetate (less than 1%), and the starting ketones, by n.m.r. spectral comparisons with authentic samples. No *endo*-bicyclo-[2.2.0]hex-2-yl acetate could be observed.

endo-Bicyclo[2.2.0]hexane-2-carboxylic Acid. The method of Wiberg and Hess[114] was followed to prepare this compound. Methyl *endo*-bicyclo[2.2.0]-hexane-2-carboxylate (0.2 g., 1.4 mmole) and solid potassium hydroxide (0.11 g., 2.0 mmole) were combined in 0.9 ml. of dry methanol and refluxed for 2.3 hours. The resulting reaction mixture was added to 1.5 ml. of water (0°), washed with three 1.5 ml. portions of pentane, acidified with dilute hydrochloric acid, and extracted with four 2 ml. portions of pentane. This extract was dried, concentrated at reduced pressure, and distilled through a short path column (50°/0.005 mm.) to yield 0.16 g. (91%) of a clear, colorless liquid. The infrared (page 49) and n.m.r. (page 59) spectra were recorded.

A small portion of this acid was reacted with diazomethane to produce the corresponding methyl ester. The infrared spectrum of this compound agreed with that of the starting endo isomer.

endo-Bicyclo[2.2.0]hexane-2-carbonyl Chloride. This compound was prepared by the method used above in the formation of cyclohexanecarbonyl chloride. endo-Bicyclo[2.2.0]hexane-2-carboxylic acid (0.17 g., 1.4 mmole), thionyl chloride (0.8 g., 6.8 mmole), and 1 drop of dimethylformamide were combined to give 0.17 g. (88% yield) of the desired clear, colorless liquid. This compound was used directly in the next reaction.

A small portion of the acid chloride was hydrolyzed with water and the infrared spectrum of the resulting acid agreed with that of the starting endo isomer.

endo-Bicyclo[2.2.0]hex-2-yl Methyl Ketone. This compound was prepared by the procedure used above in the formation of acetylcyclohexane from cyclohexanecarbonyl chloride. endo-Bicyclo[2.2.0]hexane-2-carbonyl chloride (0.17 g., 1.2 mmole) was combined with 25 ml. of dimethyl cadmium-benzene solution (prepared above) to yield 55 mg., 38% of a clear, colorless liquid. This product was analyzed by g.c. on a 7½' x ¼" Carbowax 20M column (20% on Chromosorb W) at a starting temperature of 125° and raised to 135° at 7 minutes. The flow rate was 60 ml./minute, the detector temperature was 240°, and the injection port temperature was 222°. One major peak was observed at 8.25 minutes. The infrared spectrum was identical with that recorded earlier (page 51), and the n.m.r. spectrum (page 63) was recorded. Integration of the n.m.r. spectrum gave a 71:29 ratio of endo- and exo-bicyclo[2.2.0]hex-2-yl methyl ketone.

Anal. Calcd. for $C_8H_{12}O$: C, 77.38; H, 9.74.

Found: C, 77.64; H, 9.81.

endo-Bicyclo[2.2.0]hex-2-yl Acetate. This compound was prepared by the procedure used above for the formation of cyclohexyl acetate. The mixture of *endo*- and *exo*-bicyclo[2.2.0]hex-2-yl methyl ketone (47 mg., 0.4 mmole), prepared above, was added to 0.214 g. (1.2 mmole) of 80% *m*-chloroperbenzoic acid in 1.6 ml. of methylene chloride. The reaction mixture, after stirring at room temperature for 3 days, yielded 48 mg. (90%) of a clear, colorless liquid. This liquid was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 100°. The flow rate was 150 ml./minute, the detector temperature was 240°, and the injection port temperature was 210°. Two major peaks were observed at 8.2 and 9.5 minutes. The collected peak at 8.2 minutes (77%) was identified by its n.m.r. spectrum (page 63) as a mixture of two products. Integration of the spectrum gave a 54:46 ratio of *endo*- and *exo*-bicyclo[2.2.0]hex-2-yl acetate. The second collected peak (23%) was identified by its n.m.r. spectrum (page 67) as a 74:26 mixture of *cis*-bicyclo[3.1.0]hex-2-yl acetate and 3-cyclohexenyl acetate by comparison with authentic samples. The product distribution for the reaction was then: 42, 35, 17, and 6%, respectively.

The mixture of *endo*- and *exo*-bicyclo[2.2.0]hex-2-yl acetate was stored in carbon tetrachloride solution for 21 days at -26°. G.c. analysis of this mixture on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 135° showed two major peaks at 5.65 (58%) and 6.1 (42%) minutes. The flow rate was 60 ml./minute, the detector temperature was 237°, and the injection port temperature was 211°. Integration of the n.m.r. spectrum gave a distribution of 22, 46, 25, and 7% respectively.

After standing another 25 days at -26° in methylene chloride, the n.m.r. spectrum integrated for a distribution of 14, 46, 31, and 9%, respectively.

3-Chlorocyclopentene. This compound was prepared by the method of Moffett[66] from 30.2 g. (0.457 mole) of cyclopentadiene to give 41.9 g. (90% yield) of crude product, which was used immediately in the next reaction. The infrared spectrum showed absorptions at 3.35(w), 3.45(sh), 3.49(s), 3.60(m), 6.20(w), 6.90(w), 7.00(w), 7.40(s), 7.70(w), 8.15(s), 9.90(s), 10.23(m), 11.05(s), 12.05(w), 12.70(w), and 13.5(s) μ.

2-Cyclopentenol. The procedure of Alder and Flock[3] was followed to prepare this compound from 44.4 g. of crude 3-chlorocyclopentene. Distillation of the crude product mixture through a 30 cm. Vigreux column gave three fractions. The middle fraction, 12.55 g., b.p. 53°/12 mm., n_D^{28} 1.4704 (lit.[3] b.p. 52°/12 mm., n_D^{20} 1.4717), was used for further work. The infrared spectrum showed absorptions at 3.09(s), 3.34(w), 3.44(sh), 3.49(m), 3.56(sh), 6.89(w), 7.38(m), 7.59(w), 8.66(w), 9.03(m), 9.59(s), 10.34(m), 10.94(w), 11.44(w), and 13.69(m) μ. The third fraction, 7.36 g., b.p. 44°/6 mm., n_D^{29} 1.4838, was identified by its n.m.r. spectrum as di(cyclopent-2-enyl) ether. It showed absorptions as multiplets centered at τ 4.2 and 5.4, and continuous absorption from τ 7.24 to 8.62.

cis-Bicyclo[3.1.0]hexan-2-ol. The method of Corey and Dawson[21] was followed to prepare this compound from 15.8 g. (0.188 mole) of 2-cyclopentenol, 84.8 g. (0.316 mole) of methylene iodide, and 30.7 g. (0.474 mole) of zinc-copper couple[91]. The product was distilled through a 30 cm. Vigreux column to give 11.66 g. (63% yield), b.p. 58-48°/7-4 mm., $n_D^{28.5}$ 1.4782 (lit.[21] 60% yield, b.p. 60-61°/10 mm.). The refractive index reported by Dauben and Berezin[27] was n_D^{25} 1.4742. G.c. analysis on a 6' x ¼" β,β -oxydipropionitrile column (10% on Chromosorb W) at 100° gave two peaks. The flow rate was 120 ml./minute, the detector temperature was 304°, and the injection port temperature was 285°. The first collected peak (6.6 minutes, 87%) was identified as the desired product. The second collected peak (7.6 minutes, 13%), when compared by n.m.r. spectral and g.c. retention times to an authentic sample[61], was found to be 3-cyclohexenol. The first peak trailed under the second, giving rise to a higher value for the latter than was actually present. The infrared (page 53) and n.m.r. (page 65) spectra were in agreement with those previously reported[21]. Integration of the n.m.r. spectrum indicated that the 3-cyclohexenol was only 6% of the product mixture.

__cis-Bicyclo[3.1.0]hex-2-yl Acetate__. This acetate was prepared by the method of Freeman, Grostic, and Raymond[39] from the crude __cis__-alcohol obtained above. The product mixture obtained in 94% yield (lit.[39] 50% yield) was analyzed by g.c. on a 6' x ¼" Carbowax 20M column at 125°. The flow rate was 60 ml./minute, the detector temperature was 237°, and the injection port temperature was 211°. Two major peaks were observed at 7.65 and 8.35 minutes. The first peak (6%) was identified as 3-cyclohexenyl acetate by n.m.r. spectral and g.c. retention time comparisons with an authentic sample[61]. The second peak (94%) was the desired product. The infrared spectrum (page 53) agreed with that previously reported[39], and the n.m.r. spectrum (page 67) was recorded.

__Bicyclo[3.1.0]hexan-2-one__. This compound was prepared by a modification of the method of Dauben and Berezin[30]. A solution of 13.5 g. (0.133 mole) of chromic anhydride in 20 ml. of distilled water was added, with cooling, over a period of 20 minutes to a mixture of 5.0 g. (51 mmole) of __cis__-bicyclo[3.1.0]hexan-2-ol (prepared above) in 20 ml. of ether. The resulting mixture was stirred at room temperature for 4 hours and worked-up by separating the layers, and extracting the aqueous layer with two 20 ml. portions of ether. The ether fractions were washed with three 15 ml. portions of saturated sodium bicarbonate solution, two 20 ml. portions of saturated sodium chloride solution, dried, concentrated at reduced pressure, and distilled through a short path column (27°/0.05 mm.). The light yellow liquid (2.44 g., 50% yield) was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 110°. The flow rate was 60 ml./minute, the detector temperature was 306°, and the injection port temperature was 289°. One major peak was observed at 5.0 minutes. The infrared (page 51) and n.m.r. (page 65) spectra were recorded.

trans-Bicyclo[3.1.0]hexan-2-ol. This compound was prepared by the method of Winstein, Friedrich, Baker, and Lin[116]. The bicyclo[3.1.0]hexan-2-one (2.4 g., 25.0 mmole), prepared above, was reduced with 14.8 g. (72.5 mmole) of freshly sublimed aluminum isopropoxide in 74 ml. of dry isopropyl alcohol by stirring at reflux for 18 hours. The reaction mixture was cooled to room temperature, 100 ml. of water added, neutralized with concentrated hydrochloric acid and extracted with five 30 ml. portions of pentane. The pentane solution was washed with 40 ml. of saturated sodium chloride solution, dried, concentrated, and distilled through a short path column (50°/0.005 mm.). The light yellow liquid (1.3 g., 53% yield) was analyzed by g.c. on a 6' x ¼" β,β'-oxydipropionitrile column (10% on Chromosorb W) at a temperature of 100°. The flow rate was 120 ml./minute, the detector temperature was 304° and the injection port temperature was 285°. Three major peaks were observed at 2.2 (33%), 7.3 (48%), and 8.3 (19%) minutes. The first peak was found to be unreacted bicyclo[3.1.0]hexan-2-one by comparison of its infrared spectrum with the starting material. The second and third peaks were trans- and cis-bicyclo[3.1.0]-hexan-2-ol present in the ratio of 72:28, respectively. The third peak was identified by n.m.r. spectral and g.c. retention time comparisons with the sample prepared above. Trailing of the second into the third peak was observed, which would decrease the relative amount of the trans-alcohol. The infrared (page 53) and n.m.r. (page 65) spectra of the collected second peak agreed with that previously reported[39].

trans-Bicyclo[3.1.0]hex-2-yl Acetate. This compound was prepared by the method previously described[39] in 65% yield from crude trans-bicyclo[3.1.0]-hexan-2-ol. The product mixture was analyzed by g.c. on a 7½' x ¼" Carbowax 20M column (20% on Chromosorb W) at a temperature of 135°. The flow rate was 60 ml./minute, the detector temperature was 237°, and the injection port temperature was 215°. One major peak appeared at 6.3 minutes, and its infrared (page 55) and n.m.r. (page 67) spectra were recorded. Integration of the n.m.r. spectrum indicated that 3-cyclohexenyl acetate was present in a trace amount, and cis-bicyclo[3.1.0]hex-2-yl acetate (12%) was present along with the desired product.

Stability of Various Acetates to m-Chlorobenzoic Acid in Methylene Chloride. The acetate (36 mg.) was stirred at room temperature for three days in the presence of m-chlorobenzoic acid (100 mg.) and 1 ml. of methylene chloride. The reaction mixture was added to 30 ml. of ether, washed with three 15 ml. portions of saturated sodium bicarbonate and 15 ml. of saturated sodium chloride, dried, concentrated at reduced pressure, and distilled through a short path column (27°/0.05 mm.). The product was analyzed by g.c. on a 6' x ¼" Carbowax 20M column (20% on Chromosorb W) at 125°. The flow rate was 60 ml./minute, the detector temperature was 238°, and the injection port temperature was 212°. The infrared spectrum was compared with that of the starting acetate. The following results were obtained.

1. With cis-Bicyclo[3.1.0]hex-2-yl Acetate. A single peak was observed at 8.35 minutes and the infrared spectrum was identical with that of the starting acetate. No rearrangement had taken place under these

conditions.

2. With trans-Bicyclo[3.1.0]hex-2-yl Acetate. No change could be observed by either g.c. analysis or infrared spectral comparisons.

3. With 3-Cyclohexenyl Acetate. A single peak was observed at 7.7 minutes and the infrared spectrum was the same as the starting acetate. No rearrangement had taken place under these conditions.

Irradiation of Dimethyl Cyclohexa-1,3-diene-1,4-dicarboxylate. A procedure patterned after that of Prinzbach, Hagemann, Hartenstein, and Kitzing[71] was used for this reaction. A solution of the diene (0.5 g.) in 600 ml. of anhydrous ether was photolyzed at room temperature under a nitrogen atmosphere using various mercury vapor lamps which were generally immersed in the solution in a water cooled quartz well. The solution was stirred magnetically until the ultraviolet absorption of the starting diene at 304 mμ diminished to a constant value. The reaction mixture was concentrated at reduced pressure and the n.m.r. spectrum of the resulting yellow oil recorded. The results of the various runs are listed in Table 1. The n.m.r. spectrum of the product obtained in runs 7 and 8 agreed with that previously published[71].

Methyl Cyclohexa-1,3-diene-1-carboxylate. The crude acid prepared in 50% yield by the method of Hunig and Kahanek[47] was treated with diazomethane in anhydrous ether. The clear, colorless product (b.p. 54°/2.1 mm.) was obtained in 24% yield. The infrared spectrum showed absorptions at 3.31(w), 3.42(w), 3.55(w), 5.85(s), 6.1(w), 6.35(w), 6.96(m), 7.16(w), 7.29(w), 7.53(w), 7.69(m), 7.86(s), 8.13(s), 8.40(w), 8.55(w), 9.0(sh), 9.15(s), 9.42(m), 10.0(w), 10.6(w), 11.4(w), 12.26(w), 12.36(w), 12.98(w), 13.22(w), 14.0(sh), and 14.35(s) μ.

TABLE 1

IRRADIATION SOURCES FOR PHOTOLYSIS OF DIMETHYL CYCLOHEXA-1,3-DIENE-1,4-DICARBOXYLATE.

Run #	Lamp	Filter	Reaction Time (hours)	Product
1	Hanovia 450 watt Type L	Vycor	4.75	decomposition
2	"	Corex	10.0	"
3	"	Pyrex	15.0	"
4	GE-AH4	none	6.0	"
5	Hanovia utility lamp 100 watt	none	35.0	"
6	"	Pyrex	No Reaction	
7	Hanovia 200 watt Type S	none	7.0	dimethyl bicyclo-[3.1.0]hex-2-ene-1,5-dicarboxylate
8	Hanovia 450 watt Type L	none	1.25	"

ACKNOWLEDGMENTS

The author wishes to express his sincere and deep appreciation to his major professor, Dr. Richard N. McDonald, for his guidance and encouragement throughout the course of this investigation. Dr. McDonald's competence in and enthusiasm for organic chemistry has made a lasting impression on the author. The author would also like to acknowledge the suggestions and assistance of the other members of the graduate chemistry faculty and his fellow graduate students.

The author would like to thank his wife, Marilyn, and his parents for their enduring confidence.

The author also wishes to thank the National Science Foundation (NSF Grant GP-4888) for its financial assistance in support of this project.

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117. The author wishes to thank Badischen Anilin and Soda-Fabrik for its gift of cyclooctatetraene.

118. The author wishes to thank Mr. Gary M. Muschik for the use of this spectrum.

119. All boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double beam recording spectrophotomer, n.m.r. spectra were determined on a Varian A-60 recording spectrometer. Ultraviolet absorption spectra were determined on a Cary Model 11 recording spectrophotometer. Analyses were performed by Gailbraith Laboratories, Inc., Knoxville, Tenn. The mass spectrum was obtained with a Bendix Time-of-Flight mass spectrometer. The gas chromatographic analyses were performed using a F and M model 500 temperature programmed gas chromatograph.

VITA

Gerald E. Davis was born in St. Joseph, Missouri on December 29, 1942, where he lived with his parents until marriage. There he attended grade school and graduated from Lafayette High School in 1960.

He entered St. Joseph Junior College in September of 1960, majoring in chemistry under the direction of Mr. E. C. Little. In September of 1962, he transfered to the University of Kansas, where he studied under the direction of Dr. C. A. Vanderwerf, department chairman. He received a Bachelor of Science degree in August of 1964.

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STUDIES IN THE CHEMISTRY OF BICYCLO[2.2.0]HEXANE

by

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B. S. in Chemistry, University of Kansas, 1964

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1968

Several methods of preparing simply substituted endo-bicyclo[2.2.0]-hexane derivatives have been investigated. A cycloaddition reaction between cis-3,4-dichlorocyclobutene (101) and dichloroketene failed to give the anticipated bicyclo[2.2.0]hexanone.

Cyclobutadieneiron tricarbonyl (24) could not be prepared by the published procedure, but by forcing the reaction and adjusting conditions, a consistent 48% yield was obtained. 2-Butenone was completely unstable to the reaction conditions necessary for decomposing 24 to generate cyclobutadiene. Vinyl acetate failed to react with cyclobutadiene, but methyl acrylate gave 3% of methyl endo-bicyclo[2.2.0]hex-5-ene-2-carboxylate (108) in the analogous reaction.

Although several acetylenic compounds have been reported to react with cyclobutadiene, 2-butynone (109) was not among those listed. This reaction proceeded to give bicyclo[2.2.0]hexa-2 5-dien-2-yl methyl ketone (110) and acetophenone (111) in 27% yield. Attempted diimide reduction of 110 resulted in complete destruction of the "Dewar benzene".

Methyl bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (114) was prepared by a known sequence of reactions. Diimide reduction proceeded in 93% yield to produce methyl endo-bicyclo[2.2.0]hexane-2-carboxylate (116). Ester 116 was found to be stable to base equilibration attempts, but acid equilibration gave methyl exo-bicyclo[2.2.0]hexane-2-carboxylate (117).

The reaction of methylsulfinyl carbanion with crude 116 followed by reduction produced a 38·62 mixture of endo- (112) and exo-bicyclo[2.2.0]hex-2-yl methyl ketone (123). Baeyer-Villiger reaction of ketones 112 and 123 gave three products. The mixture contained 91% of exo-bicyclo[2.2.0]hex-2-yl acetate (7c), 9% of cis-bicyclo[3.1.0]hex-2-yl acetate (124), and less than 1% of 3-cyclohexenyl acetate (8). No endo-bicyclo[2.2.0]hex-2-yl acetate could be detected in the product mixture.

A second pathway to the desired compounds began with endo-ester 116 which was saponified to endo-acid 129, and 129 was converted to endo-bicyclo[2.2.0]hexane-2-carbonyl chloride (130). Reaction of 130 with dimethyl cadmium produced a 71:29 mixture of ketones 112 and 123 in low yield. Baeyer-Villiger oxidation of this ketone mixture gave four products. The mixture contained 42% of endo-bicyclo[2.2.0]hex-2-yl acetate (131), 35% of 7c, 17% of 124, and 6% of 8.

After standing at -26° for 21 days in carbon tetrachloride, the 54:46 mixture of endo- and exo-acetate (131, 7c) had changed to 22% of 131, 46% of 7c, 25% of 124, and 7% of 8. After another 25 days in methylene chloride, the product distribution was 14% of 131, 46% of 7c, 31% of 124, and 9% of 8. The products of the rearrangement 124, 8 and trans-bicyclo-[3.1.0]hex-2-yl acetate (140b) were subjected to the Baeyer-Villiger reaction conditions and found to be stable. Therefore, the rearrangement products arose directly from 131. The rearrangement of endo-acetate 131 is rationalized as a concerted process.